Use in Synthesis of Microbial Arene Oxidation Products

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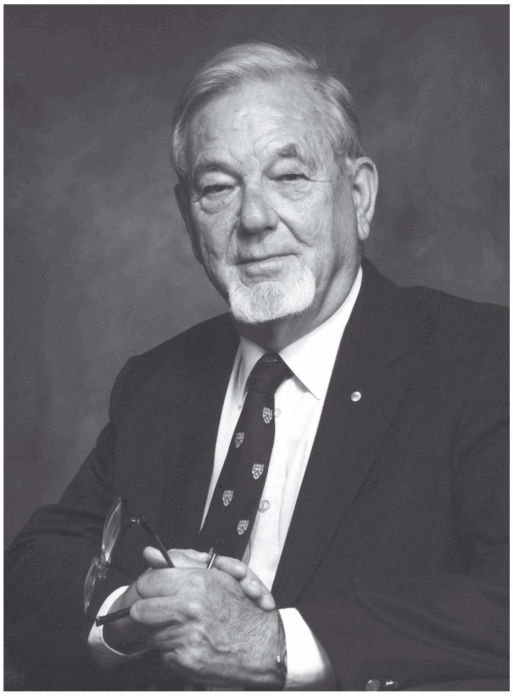
For my husband and son

ARTHUR JOHN BIRCH

3 August 1915 – 8 December 1995



Dedicated to the Memory of Professor Arthur John Birch

Abstract

This thesis is concerned with microbially derived *cis*-3,5-cyclohexadiene-1,2-dihydroxy-1-carboxylic acid and its iron tricarbonyl derivatives as precursors for the efficient and practical synthesis of useful products.

The opening chapter consists of a review of the biocatalytic *cis*-dihydroxylation process including its mechanism and applications in synthesis.

In a Chapter 2 the utility of cyclohexadiene iron tricarbonyl complexes to date is outlined, with particular focus on their preparation and reactivity. Synthetic routes towards the synthesis of the natural products gabaculine and carbazole alkaloids are described, followed by the preparation of tamiflu and general methods of decomplexation.

Chapter 3 presents the synthesis of novel iron tricarbonyl complexes and studies on their reactivity are disclosed. (Figure A.)

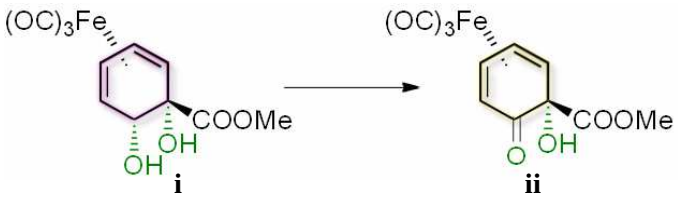
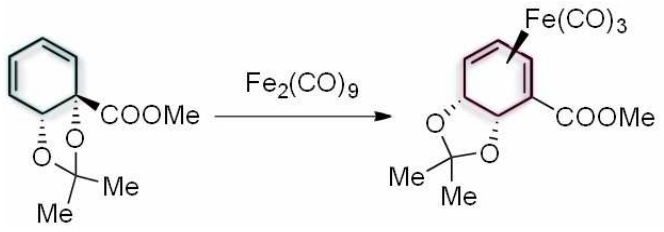


Figure A.

Chapter 4 describes the formation of a new rearrangement product of the acetonide protected iron tricarbonyl complexes. In order to validate this process, independent studies with labelled compounds have been employed. Following Myers' procedure for microbial oxidation of *p*-deutero-benzoic acid, quantities of a novel deutero-diol product were successfully prepared and used to elucidate the mechanism of the rearrangement process. (Figure B)



iii **Figure B.** **iv**

In Chapter **5** the formation of the η^5 cyclohexadienyl complexes is discussed followed by the outcome of the nucleophilic addition products. (Figure C.)

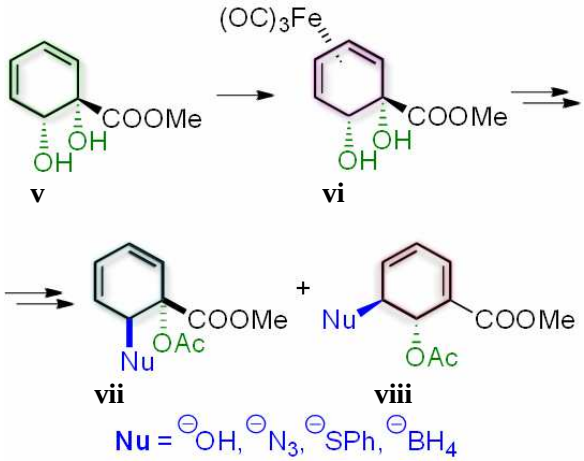


Figure C.

Chapter 7 provides detailed specific and general procedures for the synthesis of the compounds described within this thesis, along with their characterisation data. The appendices provide analytical support to this thesis and list of publications.

Each chapter includes a separate discussion of the results and Chapter **6** provides an overall summary and suggestions for possible future work.

Acknowledgement

First and foremost, I would like to thank my supervisor Dr Simon E. Lewis for the opportunity to work on such a challenging and exciting project. I would like to thank him for all his help, guidance, and encouragement over the last three years. I am grateful for being given the opportunity to work in his group.

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A special thanks must go Barbara, Robert, Primula, Sarah, Ahmad, and Liz for all the support and kindness they have shown me during my PhD life.

I'd also like to thank all the support staff at Chemistry Department, without whom data wouldn't have been compiled. I'd like to thank Dr John Lowe for assistance with NMR work, Dr Anneke Lubben for help with mass spectral analyses, and Dr Mary Mahon, Dr Gabriele Kociok-Köhn and Dr Andrew Johnson for X-ray crystallographic analysis and Dr Liana C. Allen and Dr Hannah Mauytum for help with chiral HPLC.

I thank the EPSRC, the University of Bath, CIKTN and OSI Prosidion for the financial support.

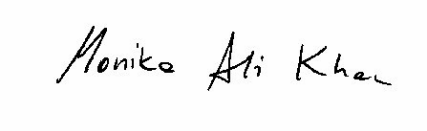
Finally, I would like to express my gratefulness to my family. They were more than patient during my many evenings of absence and preoccupation while in the lab. Special thanks go to my husband for his selfless sacrifices, and for everything he did for me along this way. Thanks to Samir. He deserved more time in the play areas with me.

I dedicate this thesis to my family, to my husband Hamid, my son Samir, my Mother Emilia and sister Magda and to the memory of my Grandmother Kazimiera Wilińska. I wish she could have seen this.

Declaration

I certify that this thesis which now I submit for the award of the DPhil/PhD degree is the result of my own work and all work done in collaboration is explicitly acknowledged in the text.

Monika Ali Khan



CONTENTS

Abbreviations

Å	angstrom
Ac	acetyl group
AcOH	acetic acid
Ac_2O	acetic anhydride
abs	absolute
AIBN	azobisisobutyronitrile
aq.	aqueous
Ar	aromatic
Bn	benzyl
Boc	*tert*-Butyloxycarbonyl
BPDO	biphenyl dioxygenase
br	broad
Bu	butyl
BZDO	benzoate 1,2-dioxygenase
BZDOS	benzoate 1,2-dioxygenase system
°C	degrees celsius
CAN	cerium(IV) ammonium nitrate
cat.	catalytic quantity
CI	chemical ionisation
conc.	concentrated
cy	cyclohexyl
C_2	180° rotation, symmetry element
δ	chemical shift in parts per million
Δ	difference in value (of chemical shift)
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane

DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
DHCDC	(1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid
DHDC	5,6-*cis*-dihydroxycyclohexa-1,3-diene
DHDC-DA	5,6-*cis*-dihydroxycyclohexa-1,3-diene diacetate,
DHCD	*cis*-3,5-cyclohexadiene-1,2-diol
DMAP	4-Dimethylaminopyridine
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
dd	doublet of doublets
dec.	decomposed
dil.	diluted
dt	doublet of triplets
ee	enantiomeric excess
EI	electron impact
EDG	electron donating group
EWG	electron withdrawing group
eq.	equivalent(s)
ES	electrospray
et al.	*et alii* (Latin), and others
Et_2O	diethyl ether
EtOAc	ethyl acetate
EtOH	ethanol
g	gram
GABA-T	gamma-aminobutyric acid-Transaminase
h	hour
HMDS	1,1,1,3,3,3-hexamethyldisiliazane
HPLC	high Performance Liquid Chromatography

HRMS	high Resolution Mass Spectrometry
Hz	hertz
IR	infrared
ITC	iron tricarbonyl
J	coupling constant
kg	kilogram(s)
KO^{t}Bu	potassium *tert*-butoxide
L	litre(s)
LA	Lewis acid
m	meta
m	multiplet
M	molar
*m*CPBA	*meta*-chloroperoxybenzoic acid
Me	methyl
MeCN	acetonitrile
CH_3OD	methanol-d_4
mg	milligram
MHz	mega Hertz
mmol	millimole
min	minute(s)
mL	millilitre
MOM	methoxymethyl
mp	melting point
MS	molecular sieves, mass spectrometry
MsCl	methanesulfonyl chloride
MTPA	*α*-methoxy-*α*-trifluoromethylphenylacetic acid
MW	molecular weight
m/z	mass to charge ratio
NAD(P)H	nicotinamide adenine dinucleotide (reduced form)
NDA	nitroso Diels-Alder

NDO	naphthalene 1,2-dioxygenase
NLO	organic nonlinear optical
nm	nanometre
NMR	nuclear magnetic resonance
o	ortho
p	para
P(DHDC-DA)	the polymer of 5,6-*cis*-dihydroxycyclohexa-1,3-diene diacetate
PDO	phthalate dioxygenase
PDS	phthalate dioxygenase system
Ph	phenyl
$PhI(OPiv)_2$	bis(*tert*-butylcarbonyloxy)iodobenzene
Phth	phthaloyl
PMB	*p*-methoxybenzyl
ppm	parts per million
PPP	polymer polyparaphenylene
Pr	propyl
^{i}Pr	*iso*-propyl
^{n}Pr	*normal*-propyl
PTAD	4-phenyl-1,2,4-triazoline-3,5-dione
PTSA	*p*-toluenesulfonic acid
Py	pyridine
q	quartet
quin	quintet
R	generic substituent
R_f	retention factor (chromatography)
$Rh_2(esp)_2$	bis[rhodium(*α*,*α*,*α′*,*α′*-tetramethyl-1,3-benzenedipropionic acid)]
rt	room temperature
s	singlet

sat.	saturated
SES	2-(trimethylsilyl)ethanesulfonyl
sol.	solution
t	triplet
td	triplet of doublets
TBAF	tetra-*n*-butylammonium fluoride
TBME	methyl *tert*-butyl ether
TBDMS	*tert*-butyldimethyl silyl
TBDMSCl	*tert*-butyldimethyl silylchloride
TCICA	trichloroisocyanuric acid
TDO	toluene dioxygenase
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
TLC	thin layer chromatography
TMANO	trimethylamine *N*-oxide
TMEDA	*N,N'*-tetramethylene diamine
TMS	trimethylsilyl, tertamethylsilane
TPA	tris(2-pyridylmethyl)-amine
Ts	*p*-methylphenylsulfonyl
UV	ultraviolet
v	wavenumber

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Chapter 1
Introduction

Chapter 1. INTRODUCTION

Iron, element 26 in the periodic table, is the fourth most abundant element and the second most abundant metal after aluminium in the earth's crust. Metal ions can serve in biological systems in many different ways depending on the distance between them and their oxidation state – one example is as sites at which enzyme catalysis occurs.[1] It is certain that billions of years ago the environment was anaerobic and sulphur and iron could form the first ever catalysts provided by Nature, proteins containing iron-sulphur (Fe−S) clusters.[2]

1.1 Rieske non-heme iron oxygenases

These enzymes are classified according to the properties of their electron transfer components, and it has been shown that the catalytic sites (α−subunits) of all Rieske non-heme iron oxygenases are very similar as a consequence of their evolution. In general the classification is correlated to the substrates oxidized by the members. The family of Benzoate oxygenases consists of enzymes that oxidize aromatic carboxylic acids (benzoate, 2-chlorobenzoate, toluate, anthranilate, isopropylbenzoate, trichlophenoxyacetate).[3]

1.2 Arene cis-dihydroxylation

It has been found that aromatic hydrocarbons can be utilized as the sole carbon source by certain bacteria under aerobic conditions. Biodegradation is initiated by bacterial Rieske non-heme iron dioxygenases (RO) with molecular oxygen, yielding the corresponding *cis*-diols, which are subsequently oxidized by catechol dioxygenases. Therefore organisms expressing Rieske dioxygenases can play an important role in bioremediation of serious environmental pollutants.[3,4,5,6]

The most studied dioxygenases are toluene dioxygenase (TDO), benzene dioxygenase (BDO), naphthalene 1,2-dioxygenase (NDO), phthalate dioxygenase (PDO), anthranilate 1,2-dioxygenase (ADO), and benzoate 1,2-dioxygenase (BZDO).[7]

The first crystal structure of an arene dioxygenase to be reported was for NDO, which was solved in 1998. The Rieske dioxygenases are an α_3 or $\alpha_3\beta_3$ hexamers. It is believed that in some cases beta subunits stabilized the alpha subunits. In most examples, the enzyme consists of three components (a) a flavoprotein reductase containing iron-sulphur cluster; (b) a Rieske [2Fe−2S] ferrodoxin; (c) an oxygenase component accommodating a Rieske [2Fe−2S] cluster coordinated by Cys-81, Cys-101, His-83, and His-104 and a mononuclear iron(II) centre which is coordinated by His-208, His-213, Asp-362 and a water molecule.[8,9] This model is illustrated in Figure **1**.

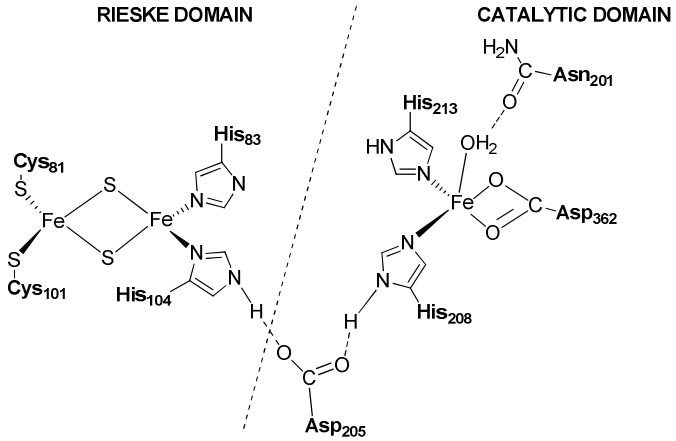
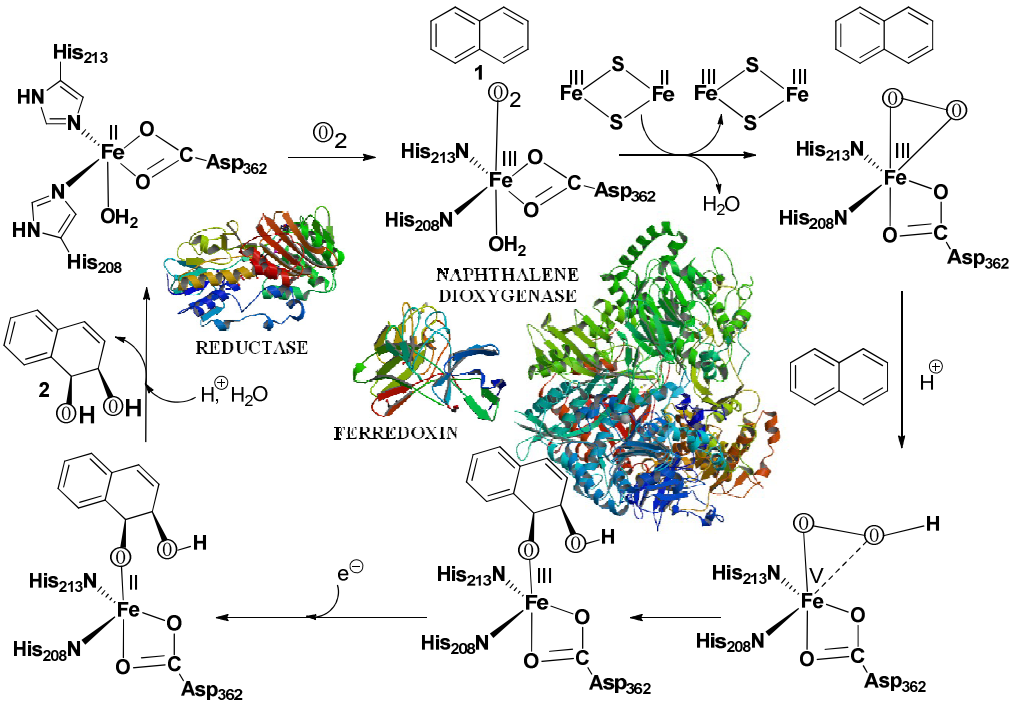


Figure 1 Two metal centres of naphthalene 1,2-dioxygenase linked by Asp205.

1.3 Mechanism of cis-dihydroxylation

The redox centres are located on the α-subunit of the oxygenase. The initial steps are not fully understood but involve movement of electrons from NAD(P)H, which are removed by the reductase and transferred to the ferredoxin. Then electrons are transferred from the ferredoxin to the Rieske domain of the oxygenase, and then molecular oxygen is bound in the active site of the catalytic domain followed by complexation of an aromatic substrate. Electrons are transferred from the oxygenase Rieske domain to the catalytic mononuclear iron and *cis*-dihydoxylated product is formed.[10,11,12] The proposed mechanism is depicted in Scheme **1**.

In addition to naphthalene NDO is known to oxidize over 30 different aromatic compounds, and the majority of the products are enantiomerically pure. One major focus of Rieske arene dioxygenase research is generation of chiral *cis*-dihydrodiols as starting materials for synthesis.[3,8]



Scheme 1 Proposed Catalytic Cycle for Naphthalene *cis*-Dihydroxylation.

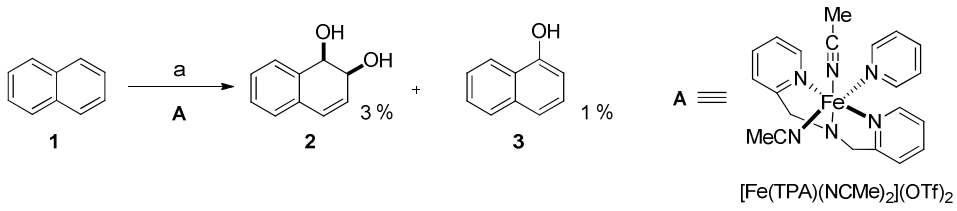
Dihydroxylation catalyzed by Naphthalene Dioxygenase. Image shows NADH-dependent ferredoxin reductase component in biphenyl dioxygenase (Protein Data Bank no. 1F3P), biphenyl reductase ferredoxin (Protein Data Bank no. 1FQT), and naphthalene dioxygenase (Protein Data Bank no. 1NDO). Symbol O_2 means ^{18}O-labelled oxygen.

The Rieske dioxygenases have a mononuclear iron active site coordinated to a "2-Histidine-1-carboxylate facial triad", and a few researchers have employed *N*-acylated dipyridin-2-ylmethylamine ligands (R-DPAH)[13] and tetraalkylcyclam complexes[14] to mimic the action of the NDO active site.[15,16]

1.4 Non-enzymatic approaches to arene dihydroxylation

1,2-*syn* diols are very common motifs in natural products and important intermediates in organic synthesis. Arene dioxygenases are selective towards a small range of aromatic hydrocarbons, which is the major problem in their applicability. Also, biotransformations are often difficult to control with low accessibility to the microorganisms and low selectivity throughout substrates. In response several research groups have address the problem of an alternative method of arene dihydroxylation able to mimic natural enzymes.

Very recently (2009) Que *et al.* have reported the first non-heme iron complex that catalyses the *cis*-dihydroxylation of naphthalene.[15] Scheme **2**.

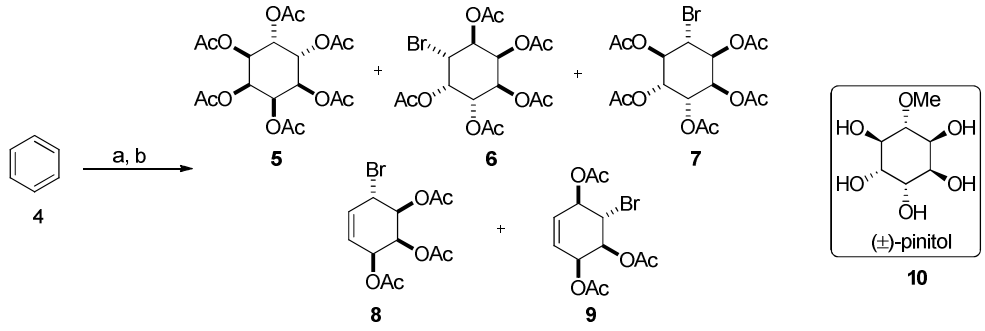


Scheme 2 Dihydroxylation of naphthalene with iron catalyst.

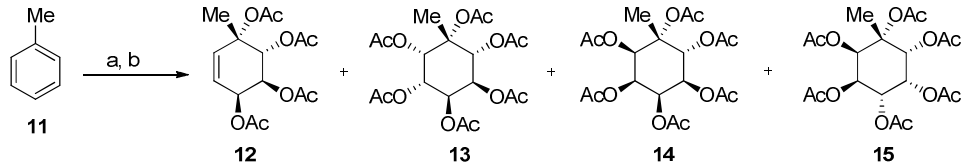
Reagents and Conditions. (a) **A** (0.5 mol%), 10.0 equiv. H_2O_2, CH_3CN, 4h, rt; TPA=tris(2-pyridylmethyl)-amine.

Napthalene was oxidised in the presence of catalyst **A** and hydrogen peroxide in CH_3CN, albeit the yield was very low. ^{18}O labelling studies have shown that the water-assisted mechanism is highly possible with initial formation of low spin Fe^{III}-OOH species, further cleaved by water to the reactive *cis*-HO-Fe^{V}=O oxidant responsible for *cis*-dihydroxylation of naphthalene.[15]

Motherwell *et al.* have also looked at alternative dihydroxylations of aromatic compounds.[17] Their work was based on prior reports from Kochi and Wallis.[18] Catalytic photoinduced charge transfer osmylation of benzene in the presence of sodium bromate or barium chlorate followed by treatment with acetic anhydride led to the mixture of cyclitols and a key intermediate **6** for the synthesis of (±)-pinitol **10**.[19]

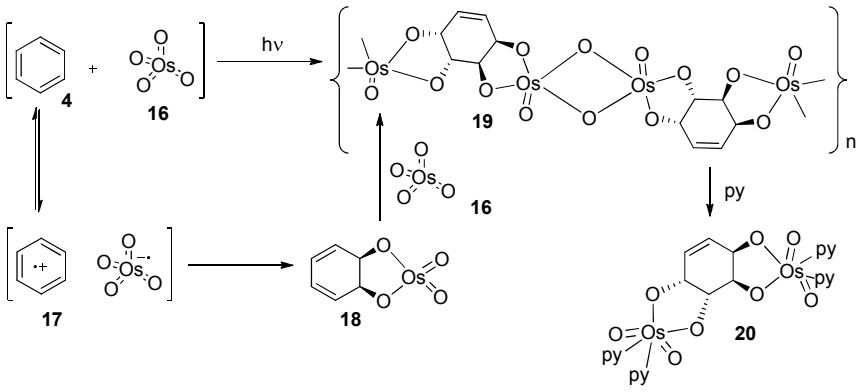


Scheme 3 Catalytic photoinduced charge-transfer osmylation of benzene.
Reagents and Conditions. (a) OsO_4 (cat.), h*v*, $NaBrO_3$ (0.22 M), 45 ℃; (b) AcOH, Ac_2O, (**5**) 7,7%, **6**:**7**, 5:11, 18.8%, **8**:**9**, 1:5, 2.3%.



Scheme 4 Catalytic photoinduced charge-transfer osmylation of toluene.
Reagents and Conditions. (a) OsO_4 (cat.), hv, $Ba(ClO_3)_2$ (0.22 M); (b) Ac_2O, Et_3N, DMAP; (**12**) 2.2%, **13**:**14**:**15** (2:1:1) 10.8%.

The overall yield of catalytic osmylation of toluene was achieved in 13% without cleavage of the carbocyclic ring. The proposed mechanism involves formation an ion pair **17** under photochemically induced charge transfer conditions, from benzene to OsO_4, which subsequently collapses to the mixture of osmate ester of benzene diol **18**; this is osmylated further to give polymeric *anti* thermal product **19**. Addition of pyridine delivered isolable monomeric product **20**.



Scheme 5 Proposed mechanism of catalytic photoinduced charge-transfer osmylation (adapted from reference[17]).

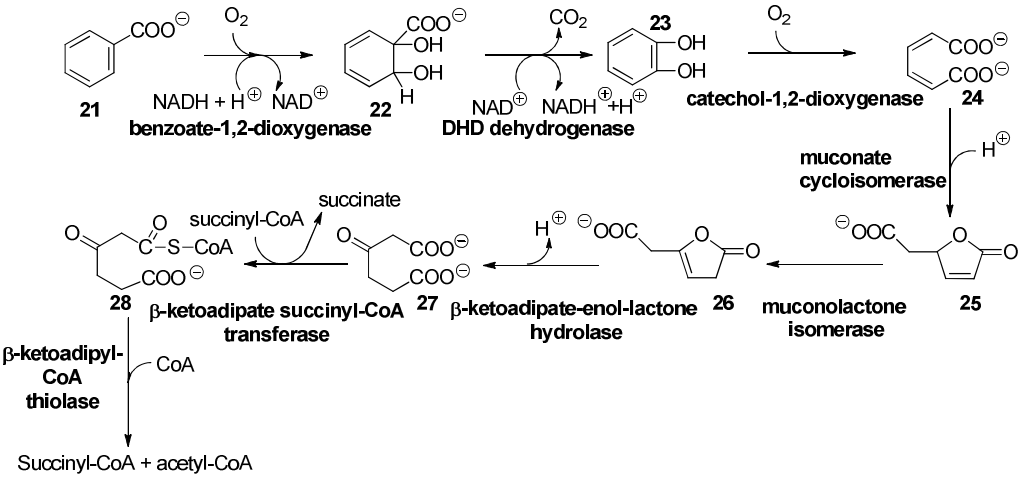
1.5 Degradation of benzoate

Many microorganisms can utilize aromatic compounds as a source of carbon. The microbial degradation of aromatic compounds has tremendous practical significance. The aromatic ring structure is degraded and the products are converted to compounds that can enter central metabolic pathways to provide a carbon source and energy. Most soil bacteria can further degrade the *cis*-diol products of arene dioxygenases with dihydrodiol dehydrogenases to yield ring opened products.[20,21,22]

The β-ketoadipate pathway is widely spread among taxonomically diverse bacteria and fungi. It plays an important role in the degradation of environmental

pollutants and naturally occurring aromatic compounds, e.g. those derived from lignins.[23]

In the specific case of *R. eutrophus* B9, the organism central to the work in this thesis, benzoate is degraded via the *ortho*-cleavage pathway to yield 1,2-dihydroxybenzoate **22**, which is converted to catechol **23** by a DHD dehydrogenase. This compound is then degraded with catechol-1,2-dioxygenase to *cis*,*cis*-muconate **24**. After several sequential inductions (each enzyme in the pathway is inducible by its specific substrate) succinyl-CoA and acetyl CoA are delivered (Scheme **6**). It is important to point out that wild-type organism utilizes benzoate by the *β*-ketoadipate pathway fully, whereas the blocked B9 mutant has an inactivated DHD dehydrogenase and so can be easily cultured to provide benzoate *cis*-1,2-dihydrodiol **22** in high-space time yield from the whole-cell fermentation.



Scheme 6 The *β*–ketoadipate pathway (the *ortho*-cleavage pathway) for the degradation of benzoate in *R*. *eutrophus*
(adapted from reference[24]).

1.5.1 Boyd's Model

Boyd *et al.* have derived a very useful method to predict the outcome of dihydroxylation of mono- and 1,4-disubstituted benzene substrates and in most cases the obtained product is an enantiometrically pure *cis*-2,3-diol.[25]

In monosubstitued arenes (R_S = H) good facial selectivity for the dioxygenase-mediated dihydroxylation is observed, with *e.e.* ≈ 100%, since all R_L substituents were significantly larger than a hydrogen atom. The notable exception, where a significant decrease in the *e.e.* value was observed, was for fluorobenzene.

For 1,4-disubstituted arenes, the size of the substituents is again the major factor in the prediction of which product will be formed.[26] In instances where the two substituents are of similar size, the *e.e.* values are eroded.

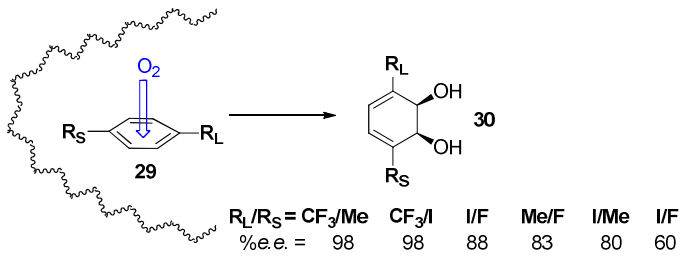
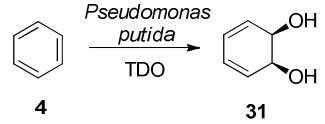


Figure 2 Boyd's model for predicting the regio- and stereochemical outcome of microbial oxidation of monocyclic aromatics.

1.6 Diversity of metabolites

Since the first investigation of the arene dioxygenase by Gibson in the late 1960s[27,3] the reaction has been intensively studied.[28,3,29,30,30,31,32,33-36]

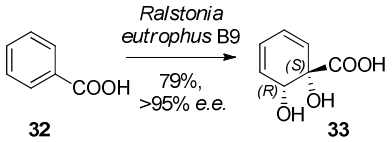
Certain strains of the common bacterium *Pseudomonas putida* are able to synthesize *cis*-3,5-cyclohexadiene-1,2-diol (DHCD) **31** from benzene by oxidation with toluene dioxygenase (TDO) and recently this enzyme was expressed in recombinant bacteria.[37]



Scheme 7 Microbial oxidation of benzene with *P. putida.*

The *ortho-meta* dihydroxylation is by far the most common regiochemical outcome in most arene-metabolising bacteria and relays very well onto Boyd's model to deliver *cis*-configured dihydrodiols.

In 1971, Reiner and Hegeman isolated a mutant strain of *Ralstonia eutrophus* (strain B9, formerly known as *Alcaligenes eutrophus*) that oxidized benzoic acid **32** to (1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid (DHCDC) **33**.[38] In contrast this is a rare example of *ipso-ortho* oxidation, also with a reversed sense of absolute enantioinduction.

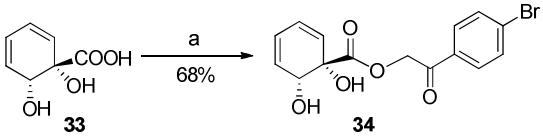


Scheme 8 Microbial oxidation of benzoic acid with *R.eutrophus* B9.

In order to avoid complete degradation of the DHCDC product **33**, this mutant microorganism lacks a working version of the enzyme dihydroxydiol dehydrogenase. Myers *et al.* have demonstrated that modification of the original procedure reported by Reiner *et al.* can deliver DHCDC **33** on a multihundred gram scale (and as a single enantiomer).[39]

Mono- and disubstituted benzoic acids have been found to be acceptable substrates for benzoate 1,2-dioxygenase. It was found that *meta*- substituted benzoic acids have comparatively high turnover rates, whereas the *ortho*- and *para*-substituted ones underwent dihydroxylation only with fluorine as a substituent.[40,31,41]

In 1987, Ribbons and Williams showed that mutant *Pseudomonas putida* JT103, could also oxidize benzoic acid and its derivatives to the corresponding vicinal *cis*-diols such as DHCDC.[42] Furthermore, *P. putida* KTSY01 showed the ability to oxidize benzoate to DHCDC.[43] In 1995, Widdowson and coworkers reported the synthesis of **33** with *P. putida* U103.[44] Also they assigned for the first time the stereochemistry and absolute configuration of *cis*-diol acid **33** (1*S*,2*R*), by X-Ray analysis of its *p*-brombenzoylmethyl ester derivative **34**. (Scheme **9**, Figure **3**)



Scheme 9 Formation of *p*-bromobenzoylmethyl ester of **34**.

Reagents and Conditions: (a) **33**, Et_3N (2.15 mmol), acetone, *p*-bromobenzoyl methyl bromide in acetone (1.2 equiv.), 3 h, rt., 68%.

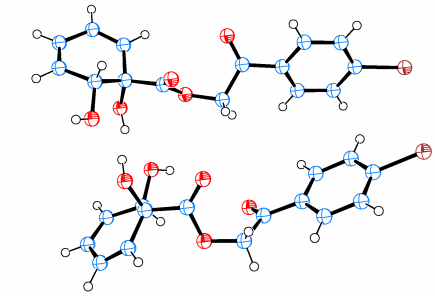
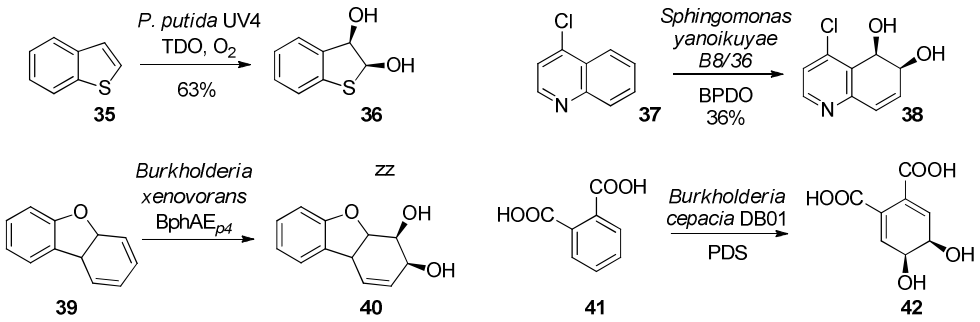


Figure 3 Crystal structure of **34**

The benzoate 1,2-dioxygenase systems (BZDO) from *Pseudomonas putida* mt-2 and *Acinetobacter* sp. Strain ADP1 have also been purified and characterised.[45,46]

As a representative example of the diversity of metabolites, in 2012, D. R. Boyd and coworkers investigated microbial oxidations (*P. putida* UV4) of benzo[b]thiophenes to give product **36**.[47] Sylvestre *et al.* demonstrated that the scope of the biooxidation by biphenyl dioxygenases of mutant strains can be expanded to various substrates for example to dibenzofuran.[48] However, *P. Putida* UV4 was not so effective during oxidation of 4-chloroquinoline compared with *Sphingomonas yanoikuyae* B8/36.[49,50] Dihydroxylation of phthalate **41** was

completed with phthalate dioxygenase system (PDS) from *Burkholderia cepacia* DB01.[51]



Scheme 10 Some examples of reactions catalyzed by Rieske Oxygenases from wide range of microorganisms.

1.7 Application in synthesis

Microbial 2,3-dihydroxylation products (DHCD) have been used systematically in the synthesis of metalloorganic intermediates, inositols and many natural products.[39,52,53,54]

Diol acid **33** has seen isolated previous reports of use in organic synthesis. In 2005, Myers and coworkers reported syntheses of important natural and unnatural tetracycline antibiotics.[55,56] A few years later Parker *et al.* have provided an efficient synthesis of carba-*β*-L-fructopyranose in seven steps from **33**.[57] In contrast Mihovilovic *et al.* have published the results of a study on intramolecular Diels–Alder derivatives of **33**.[58,59] In 2011, Hudlický reported the synthesis of idesolide in just five steps from benzoic acid.[60] Recently Lewis and coworkers have demonstrated the use of microbial diol acid **33** in syntheses of natural product zeylenols and zeylenones as well as (+)-grandifloracin[61,62], the bromosubstituted derivative of DHCDC[63] and a CpCo complex **48**[64]. Figure **4**.

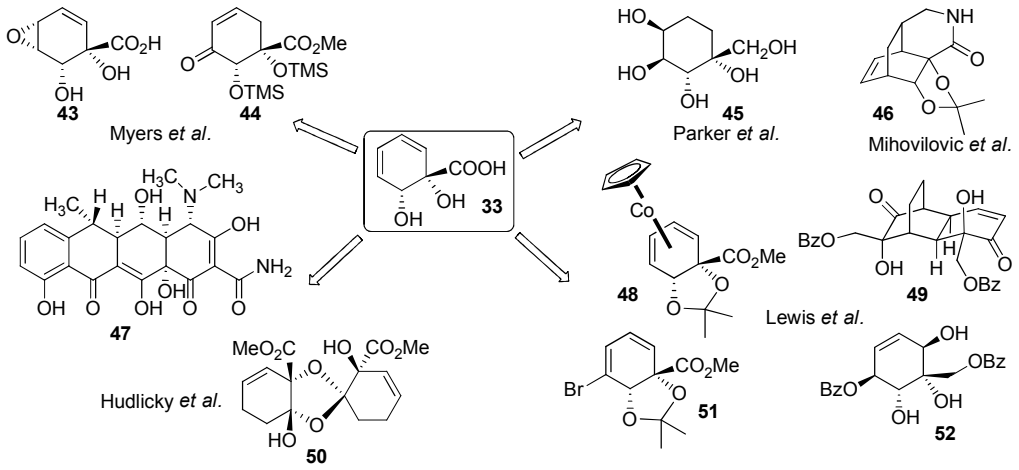


Figure 4 Novel products delivered from microbial oxidation *cis*-diol **33**.

In recent years, the more common microbially derived *cis*-2,3-diols were exhaustively explored in order to access natural and unnatural cyclitols, conduramines, inositols, carbohydrates, and the anti-HIV agent indinavir.[26,65,66,67,50,68,69,70,71]

Specifically highlighted examples include oseltamivir along with codeine **62**, balanol (**59**) and 7-deoxypancratistatin (**57**) and epibatidine (**56**), hexacyclinol (**58**),[72] connatusin A (**61**),[73] narseronine (**63**)[74] which were obtained from enzymatically derived *cis*-bromo, iodo- or ethoxycarbonyl dihydrodiol metabolites.[75,76,77]

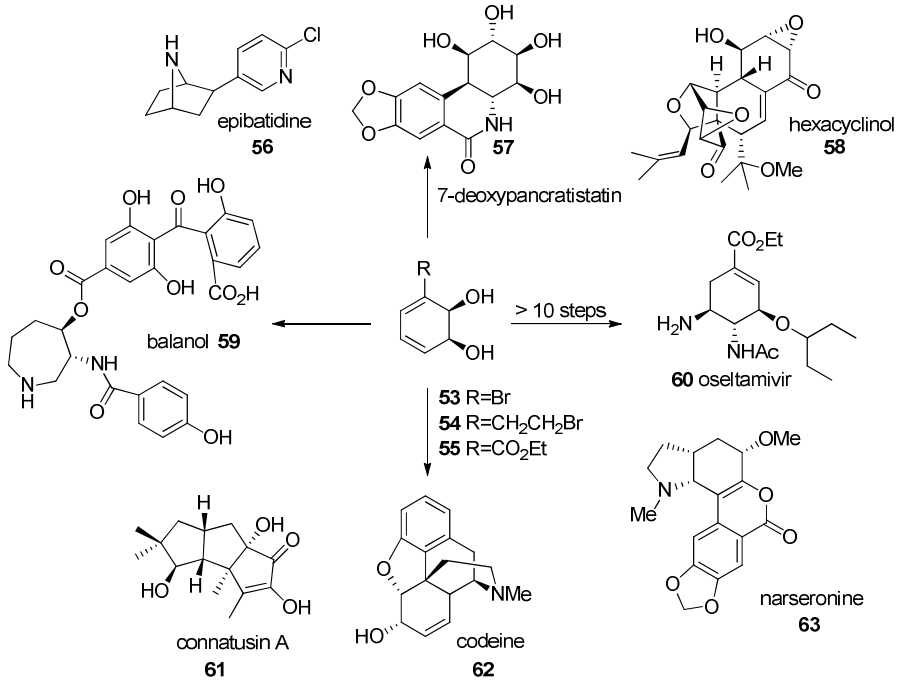
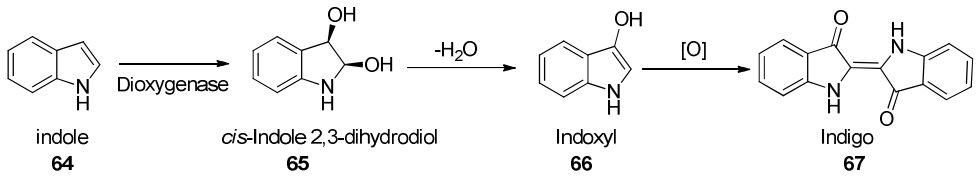


Figure 5 Syntheses of 7-deoxypancratistatin, balanol, codeine, oseltamivir, epibatidine, hexacyclinol, connatusin A, and narseronine.

There have been many other applications to use dioxygenases in organic chemistry.[78] The most unusual is the oxidation of indole **64** to the blue jean dye indigo **67** by *Pseudomonas indoloxidans*.[79,80,81]

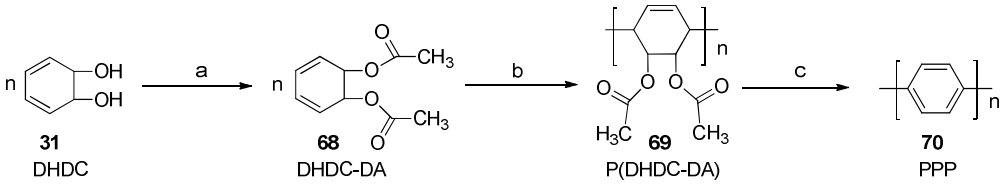


Scheme 11 Oxidation of indole by Naphthalene Dioxygenase, the remaining reactions occur spontaneously in air.

This process was later optimized to an industrial-scale fermentation.

Novel methods into production of polymers under environmentally friendly conditions have been intensively studied.[82,83] In 1988, Ballard *et al*., have

developed polymerization process using derivatives of *cis*-dihydrocatechols (DHDC) obtained from microbial fermentation of benzene.[84] The yield was only 60% but Xu *et al*., have prepared conducting polymer polyparaphenylene (PPP) by Ballard *et al*.'s method from purified monomer **31**.[85] Scheme **12**



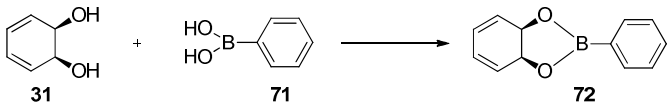
Scheme 12 Synthesis of PPP from *cis*-dihydrocatechol **31**.

Reagents and conditions: (a) DHDC, acetic anhydride, −10 ℃, 2 h then warm up, 92% after distillation; (b) DHDC-DA (51.0 mmol), AIBN (0.03 mmol), THF, 70 ℃, 72 h; (c) P(DHDC-DA), 270 ℃ to 300 ℃ with 10 ℃ interval for 1 h u nder N_2.

1.8 Isolation of cis-dihydrodiols

Most *cis*-dihydrodiols are highly water-soluble and, in many cases, inherently unstable. Therefore, the isolation process of microbial oxidation products (*cis*-DHDC) can be problematic. Usually the *cis*-dihydrodiols are extracted several times with ethyl acetate, and after concentration they can be stored at −78 ℃ without traces of phenols or acids, which can catalytically lead to rearomatization products.

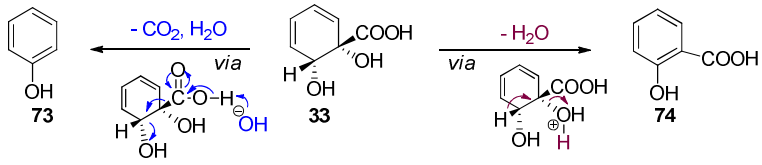
One approach to long term storage is that of Herbert *et al.*, who have applied the method of formation of unsoluble phenylboronate complexes, which can be hydrolysed and reused again after recrystalization.[83,64,86]



Scheme 13 Formation of phenylboronate complex **72.**

Some methods of purification of dihydroxylation products required use of charcoal or zeolite and after binding DHCD successively passing through the column an aqueous solution to remove water soluble components (DNA, proteins) followed by *e.g.* methanol.[87]

It must be kept in mind that **33** itself is unstable upon prolonged exposure to air and moisture at room temperature, which leads to rearomatization products phenol **73** and salicylic acid **74**.



Scheme 14 Degradation of *cis*-3,5-cyclohexadiene-1,2-diol **33**.

1.9 Conclusion

In this chapter I have described the production of microbial diols from aromatic precursors by different types of dioxygenases, including mechanistic investigations of bio-oxidation process. I have added information about theirs applications towards syntheses of several natural products and polymers. More work must be done in order to recover microbial oxidation products and strain development to access new enantiomerically pure building blocks on industrial scale.

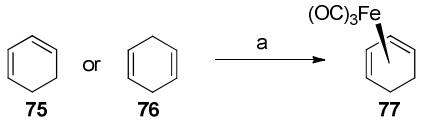
Chapter 2

Cyclohexadienyl complexes in organic synthesis

CHAPTER 2. CYCLOHEXADIENYL COMPLEXES IN ORGANIC SYNTHESIS

The chemistry of organoiron complexation dates back to 1930, when Reihlen and co-workers[88] described for the first time the isolation of an acyclic (η^4-buta-1,3-diene)tricarbonyliron(0) complex, when iron pentacarbonyl reacts with butadiene in an autoclave. Several years later after the discovery of ferrocene[89,90,91], the synthesis of butadiene-iron tricarbonyl was reinvestigated.[92]

In 1958, Hallam and Pauson prepared[92] (η^4-cyclohexa-1,3-diene)tricarbonyl **77**, by direct reaction of $Fe(CO)_5$ with cyclohexa-1,3-diene as shown in Scheme **15**.

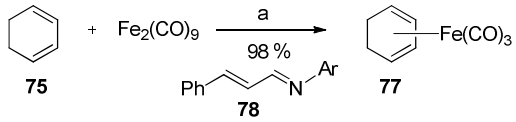


Scheme 15 Hallam and Pauson synthesis of (η^4-cyclohexa-1,3-diene)tricarbonyl complex. Reagents and Conditions. (a) $FeCO_5$, autoclave, 135 ℃, 24 h.

The scope of this complexation was improved by Arnet and Pettit[93], when they discovered that non-conjugated 1,4-dienes (*e.g*. **76**) react with pentacarbonyliron resulting in formation of *conjugated* tricarbonyl complexes. Since then a variety of substituted 1,4-cyclohexadiene ligands were delivered by Birch reduction of the corresponding aromatic precursors.[94,95]

Usually coordination of iron tricarbonyl moiety is achieved under thermal or photochemical conditions with iron pentacarbonyl, diiron nonacarbonyl or triirondodecacarbonyl in moderate yield (30%-50%). Iron tricarbonyl complexes are usually stable towards air and moisture and can be stored for several months without any significant decomposition.

Knölker *et al.* achieved complexation of 1,3-cyclohexadiene under mild conditions by using a catalytic amount of tricarbonyliron transfer reagent **78** in 98% yield[96] as shown in Scheme **16**.

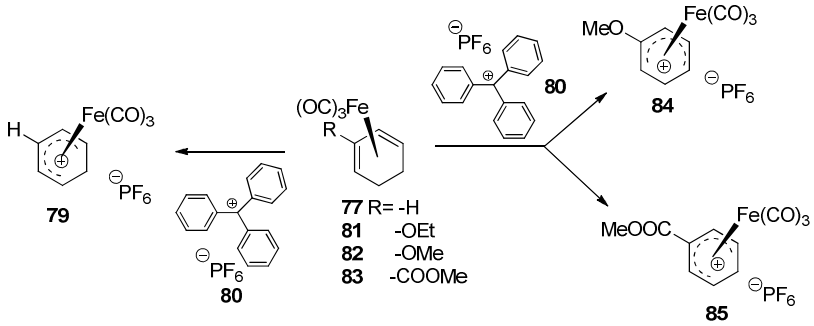


Scheme 16 Complexation of 1,3-cyclohexadiene with tricarbonyl transfer reagent **78.**
Reagents and Conditions. (a) **78** (0.125 eq), $Fe_2(CO)_9$ (1.5 equiv. based on iron), DME, 85 ℃, 16.5 h, 98%.

It must be mentioned that chiral enantiopure (η^4-1-aza-1,3-butadiene)tricarbonyl complexes can act as asymmetric catalysts and deliver enantiopure tricarbonyl iron complexes. Knölker *et al.* described the first asymmetric complexation of prochiral ligands with chiral camphor derivatives of 1-azabutadienes.[97]

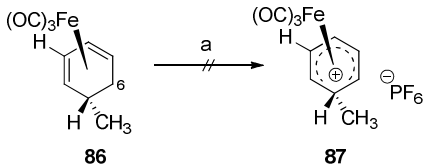
2.1 Preparation of η^5-cyclohexadienyl cationic complexes

In 1960, Fischer and Fischer reported for the first time formation of a cationic iron tricabonyl complex by hydride abstraction from a neutral complex using trityl tetrafluoroborate.[98] Various methods are available to access η^5-cyclohexedienyliron tricarbonyl intermediates from the corresponding cyclohexadieneiron tricarbonyl complexes. The most common procedure used is direct hydride abstraction from neutral (η^4-cyclohexadiene) with trityl hexafluorophosphate or trityl tetrafluoroborate[99,100,98,101,102,95] in dichloromethane. As regards regioselectivity, for 2-substituted cyclohexadiene complexes, if R is an EDG e.g. -OMe, the major product is delivered in 94% yield (isomer **84**) whereas if R is an EWG the reaction produces **85** in 95% yield.[103] Scheme **17**



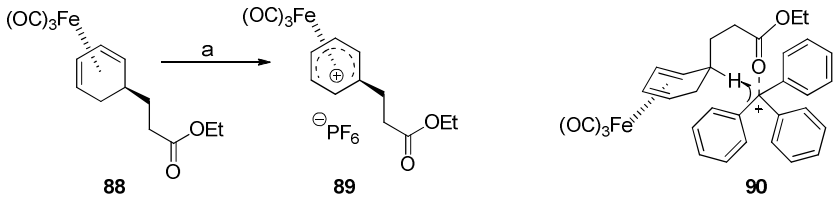
Scheme 17 Formation of cationic intermediates by trityl cation.

However, the outcome of these hydride abstraction reactions also depends on the steric effects of the starting material.[103] When a substituent is present at the C-5 carbon and *anti* to the metal, the abstraction generally does not occur. An example is shown below, wherein the complex **86**, when subjected to this methodology, failed to produce cation **87**.[104]



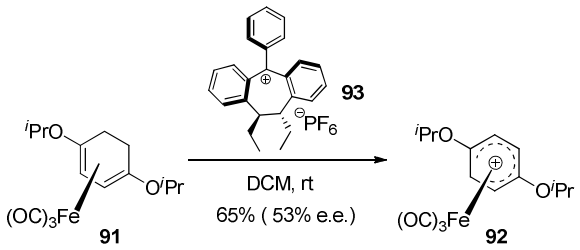
Scheme 18 Attempted formation of cationic intermediate.
Reagents and conditions: (a) trityl tetrafluoroborate, DCM, 30 min.

It is possible that the methyl group "*exo*- to" the iron tricarbonyl moiety is effectively blocking the approach of the bulky trityl cation as required for hydride abstraction at C-6. A rare exception is the report from Yeh and Wang of hydride abstraction of the most hindered *endo* C-5 hydrogen in complex **88** by triphenylcarbenium hexafluorophosphate in acetonitrile to give a air stable cation salt **89** in 84%.[105]



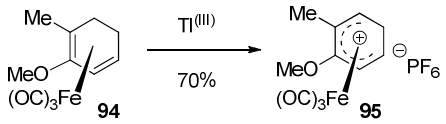
Scheme 19 Formation of cationic intermediate **89** by abstraction of hindered *endo* hydrogen. Reagents and conditions: (a) **88**, triphenylcarbenium hexafluorophosphate (1.5 equiv.) acetonitrile, 25 ℃, N_2, 8 h, 84%.

Asymmetric hydride abstraction from *meso* 1,4-dialkoxycyclohexadienyl iron carbonyl complexes by a chiral trityl cation **93** was reported by Pettus and co-workers in moderate enantioselectivities (43-53% *e.e.*). [106,107]



Scheme 20 Desymmetrisation of a *meso* iron carbonyl complex.

To avoid the problem of steric inhibition of hydride abstraction, several alternative methods were developed, such as oxidation of neutral 1-OMe, 2-OMe iron tricarbonyl complexes with thallium(III) tris(trifluoroacetate) at rt or activated DDQ-HBF_4 at −78 ℃. [108] Stephenson *et al.* have applied thallium (III) oxidation to synthesis of (±)-carvone **96** and (±)-sylvecarvone **97**.[109]



Scheme 21 Formation of cationic intermediate by thallium (III) trisfluoroacetate (TTFA).

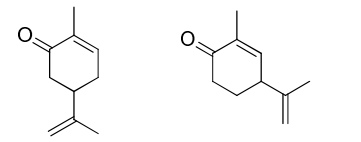
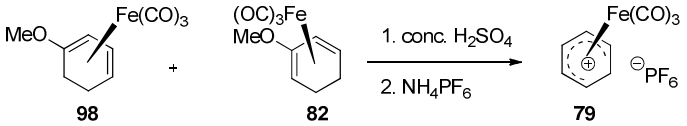


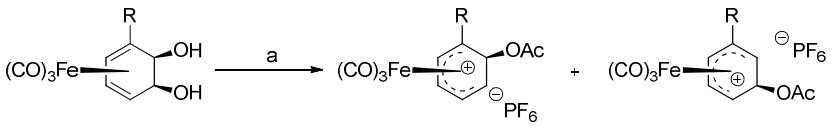
Figure 6 Structures of (±)-carvone and (±)-sylvecarvone.

Another method of preparation of η^5-cyclohexadienyl salts is by treatment of the corresponding 1- or 2-substituted hydroxy or methoxy irontricarbonyl complexes with acid.[110]



Scheme 22 Formation of cationic intermediate **79** under acidic conditions.

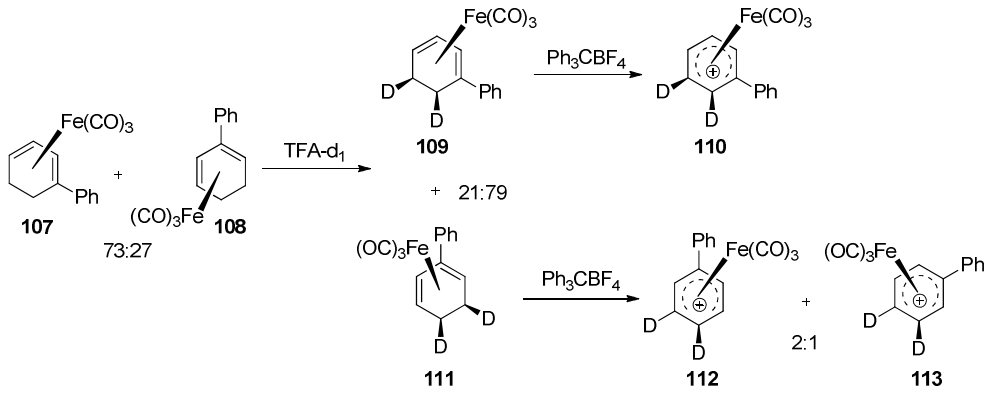
Stephenson and co-workers have examined[111] formation of complexes under acidic conditions.[28,112] It must be mentioned that these microbial diene diols were for the first time used for $Fe(CO)_3$ complexation. An arene 1,2-*cis* dihydrodiol (**99**, **100** or **101**) in acetic anhydride reacted with hexafluorophosphoric acid to give cation **102** or **103**, depending on the electronic nature of the substituent R. For instance, methoxy- and chloro- substituents predominantly lead to **102** and **104** complexes in a ratio 2:1, and 7:2 respectively, as shown in Scheme **23**. On the other hand, a trifluoromethyl substituent gave **106** as the sole product.



Scheme 23 Formation of monosubstituted cationic intermediates.
Reagents and conditions: (a) HPF_6, Ac_2O.

The mechanisms of the formation of cationic species were investigated widely for acyclic and cyclic products.[113] On treatment of a mixture of **107** and **108** with deuterated trifluoroacetic acid (TFA-d_1), a mixture of **109**-d_2 and **111**-d_2 was produced, which was separated by column chromatography on alumina. Both products were subsequently subjected to hydride abstraction by reaction with trityl tetrafluoborate.

Interestingly, in both cases, hydride was lost and two different products were produced (Scheme **24**).



Scheme 24 Labelling studies of the formation of cationic species.

In view of the above results the hydride abstraction by triphenylcarbenium cation is presumably affected by steric hindrance due to the phenyl group, and therefore the hydrogen is removed at C-5 for **109**-d_2, and at C-1 or C-4 for **111**-d_2.

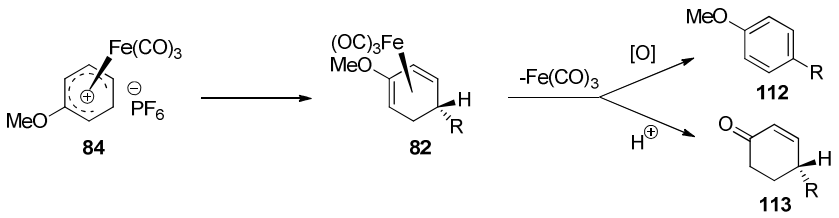
2.2 Nucleophilic additions towards (η^5-cyclohexadiene)iron tricarbonyl cations

The (η^5)-cationic cyclohexadienyl complexes are very reactive electrophiles and they react regio- and stereospecifically upon treatment with nucleophiles. The outcome of the reaction is determined by the arrangement of any substituents

and by iron tricarbonyl tripod, in which the nucleophilic addition typically proceeds by approach to the diene face *anti* to the metal due to both steric and electronic effects.

Birch *et al*. defined this strategy as "superimposed lateral control of reactivity, stereochemistry and structure".[114,115]

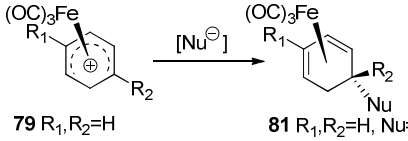
This can be demonstrated by the reaction of η^5-methoxy iron cation **84** with a nucleophile to deliver neutral iron complex **82**, which can behave differently under subsequent demetallation and dehydrogenation giving *p*-substituted anisole **112**, or under acidic hydrolysis providing the 4-substituted cyclohex-2-enone **113**.



Scheme 25 An example of superimposed lateral control of reactivity.

A wide variety of reagents have been used in nucleophilic additions to cationic (η^4-cyclohexadienyl)$Fe(CO)_3$ complexes, and this reaction has proved to be of great value in synthesis. This is a very powerful tool to carry out C-C, C-X (X=N, O, S etc.) bond formation under very mild conditions.[116]

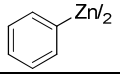
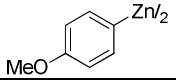
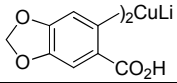
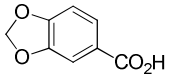
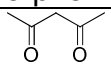
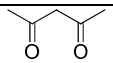
The salts readily react with a wide variety of nucleophiles such as hydroxide and alkoxyanions[117], amines, enamines[102] and ketones as enols, thiocyanate, selenocyanate and cyanate ions, halide ions, nitrite ions, azide and dithiocarbamates.[118] Alkylation with dialkylzinc, dialkylcadmium, lithium alkyls and organocuprates is also known.[119,120,121,122]

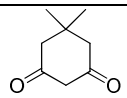
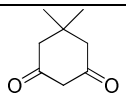
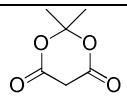
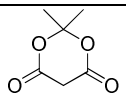
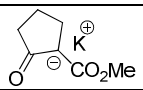
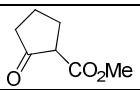


Entry **1** **79** R_1,R_2=H — **81** R_1,R_2=H, Nu=H **114a-o** Nu≠H
Entry **2** **84** R_1=OMe R_2=H — **82** R_1=OMe R_2=H Nu=H **115a-d** Nu≠H
Entry **3** **116** R_1=OMe R_2=Me — **116a-c** R_1=OMe R_2=Me
Entry **4** **117** R_1=Me R_2=H — **117a-b** R_1=Me R_2=H
Entry **5** **118** R_1=OMe R_2=Et — **118a** R_1=OMe R_2=Et

Scheme 26 Nucleophilic addition to η^5-cyclohexadienyl cations.

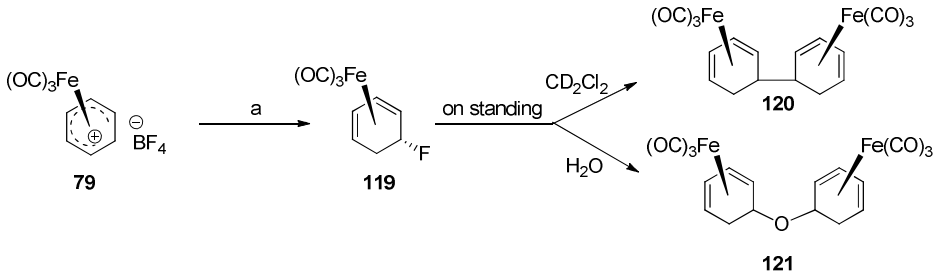
Table 1 Examples of nucleophilic addition into (η^5)-cyclohexadienyliron complexes; "-" yield not reported although product was obtained.

Nucleophile	R_1,R_2	Product Nu=	Yield
$NaBH_4$	H,H	H	23%[123]
MeLi	H,H	Me	87%[116]
Me_2CuLi	H,H	Me	80%[119]
$(CH_2{=}CHCH_2)_2Zn$	H,H	$CH_2{=}CHCH_2$	82%[123]
KCN	H,H	CN	59[123],52%[94]
NaOMe	H,H	OMe	53[123],57%[94]
$HOSi(CH_3)_3$	H,H	$OSi(CH_3)_3$	42%[117]
KOPh	H,H	OPh	64%[117]
	MeO,H	Ph	60%[124,125]
	MeO,H	*p*-MeO-Ph	61%[125]
MeLi	MeO,H	Me	94%[116]
KCN	MeO,H	CN	94%[126]
	MeO,H		26%[127]
$NaBH_4$	MeO,H	H	65%[104],88%[99], 50%[114]
$NaCH(CO_2Et)_2$	MeO,Me	$CH(CO_2Et)_2$	89%[128,129]
$NaHCO_3/H_2O$	MeO,Me	OH	90%[99]
$O(CH_2CH_2)_2NH$	MeO,Me	$O(CH_2CH_2)_2N$	65%[99]
$NaHCO_3/H_2O$	H,H	OH	75%[94]
	H,H	C_4H_8N	82%[94]
$O(CH_2CH_2)_2NH$ Morpholine	H,H	$O(CH_2CH_2)_2N$	-[94]
	H,H		93%[94]

 dimedone	H,H		79%[94]
 Meldrum's acid	MeO,H		97%[130]
	MeO,Me		93%[131]
$(CH_2{=}CHCH_2)_2Zn$	Me,H	$CH_2{=}CHCH_2$	50%[132]
$(Me_2CH)_2Zn$	Me,H	$CH_2{=}CHCH_2$	50%[132]
KI	H,H	I	9%[133]
NH_2Boc	H,H	NHBoc	83%[101]
$AgNO_2$	H,H	NO_2	-[118]
$KCH(CO_2Et)_2$	MeO,Et	$CH(CO_2Et)_2$	96%[123]
NH_4SCN	H,H	SCN	-[118]

Limited applications in surface functionalisation have also been reported in the literature, where cationic cyclohexadiene complexes are attached to a polystyrene surface in order to introduce novel polymers as new chiral stationary phases.[134,135]

There are a few examples in the literature of direct fluorination of a cationic cationic (η^5-dienyl)iron tricarbonyl complex. Attempted introduction of fluoride ion, for the purposes of forming a C-F bond was investigated by Powell and Horvath.[136] The reaction was carried out under rigorously anhydrous conditions with KF/18-crown-6 and **79** in acetonitrile. The fluoride ion was captured to give **119**, but the complex was not stable and readily loses fluoride to give C-C linked dimer **120**.



Scheme 27 An attempted introduction of fluoride nucleophile to cationic **79.**
Reagents and conditions: (a) KF/18-crown-6 or $[(Me_2N)_3S]$-$[Me_3SiF_2]$, CD_2Cl_2.

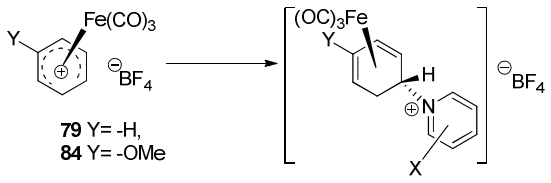
Also, formation of a C-C dimer has been observed upon reaction of **79** with oxy anions such as hydroxide[117] and with iodide.[133]

Both neutral and cationic complexes are valuable as intermediates in organic synthesis, although η^5-cyclohexadienyls are more reactive and are capable of efficent reactions with a wide variety of nucleophiles, and of S_EAr reactions with aromatic ring systems.

Methoxsubsituted cyclohexadieneiron complexes can react with strong acids (TFA), followed by anion exchange with ammonium hexafluorophosphate to provide the corresponding salts, which can be isolated. The reactivity of the 2-methoxycyclohexadienyl cation complex has been widely studied, and nucleophilic attack takes place at the C-5 position. In addition, increasing the steric congestion at C-5 on the dienyl dooes not change the preference for this carbon being attacked.[103]

Interestingly, in 2010, Adejoro *et al.* developed the reaction of pyridines and pyridine derivatives with the organometallic complexes **79** and **84** giving novel pyridino(1,4-*η*-2-methoxycyclohexa-1,3-diene) derivatives of iron tricarbonyl complexes, as shown in Scheme **28**.[137]

The reactions were performed with freshly distilled reagents before use and the reaction mixture allowed to stand at room temperature for 10 min, in acetonitrile. After solvent evaporation and several washes with petroleum ether, twelve new products were isolated (yields not reported).



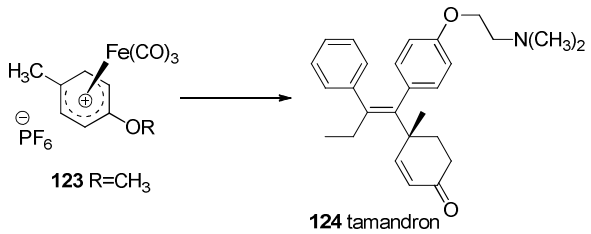
122a-f X= H, 2-Me, 3-Me, 4-Me, 4-NH_2, 4-$NH(Me)_2$

Scheme 28 Preparation of novel iron complexes with pyridines and pyridine derivatives.

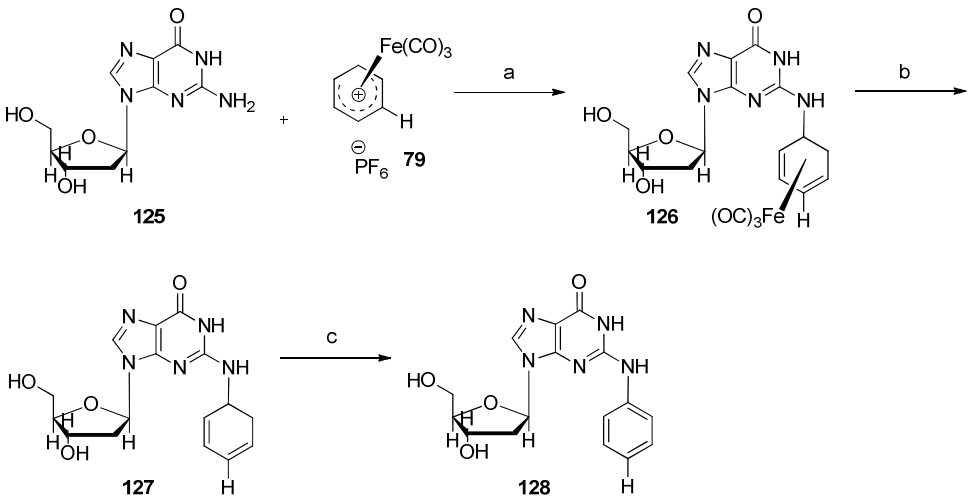
Cationic iron intermediates were also applied in the derivatization of galactosides at the C3-position, which could be useful in the preparation of new carbohydrate derivatives of biological interest.[138]

McCague and Potter have developed a novel methodology employing 2-methoxy substituted cyclohexadieneiron complexes with low-order organocopper complexes to produce an anticancer drug candidate, an analogue of tamoxifen which they refer to as tamandron.[139] Scheme **29**

Moreover, the same authors have reported synthesis of N^2-arylated nucleosides directly from the corresponding non-protected 2'-deoxyguanosine in just three steps by treatment with tricarbonyl(η^5-cyclohexadienylium)iron or tricarbonyl[η^5-2-(*n*-butyl)cyclohexadienylium]iron cations.[140] Scheme **30**



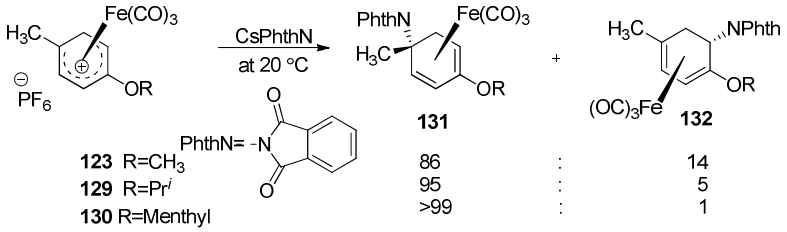
Scheme 29 McCague and Potter approach towards tamandron.



Scheme 30 Synthesis of N^2-arylated nucleosides.

Reagents and conditions: (a) 2,6-di-*tert*-butyl-4-methylpyridine, MeCN, 20 ℃; (b), Me_3NO, $MeCONMe_2$, 90 ℃; (c),$(MeCN)_2PdCl_2$, Et_3N, $MeCONMe_2$, 80 ℃

Interestingly, the caesium salt of phthalimide reacts with chiral complex **130**, prepared from *p*-(1*S*,2*R*,5*S*)-menthoxytoluene, to give the product **131** after nucleophilic addition *ipso* to the methyl substituent at the C-5 position.[141] This strategy may be applied to the synthesis of 4-methoxycyclohexadienones, important intermediates in the synthesis of the A-ring of steroid hormones, potential lead compounds for treatment of hormone-dependent cancers.

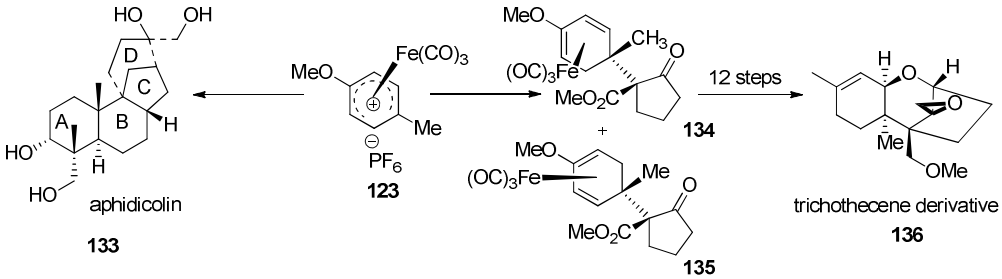


Scheme 31 Nucleophilic addition of caesium phthalimide into cationic salts at 20 ℃.

Pearson *et al.* have shown the tricarbonyl(4-methoxy-1-methylcyclohexadienylium)iron hexafluorophosphate **123** reacts at the methylated dienyl terminus with the potassium enolate of methyl 2-

oxocyclopentanecarboxylate in a regio- and stereospecific fashion, leading to two diastereoisomers, which were further converted to 12,13-epoxy-14-methoxytrichothecenes of potential biological interest.[142,143,144] Since the 12,13-epoxide is essential for pharmaceutical activity, any active synthetic analogues must contain this functionality. This methodology opens the way to a wide range of trichothecene derivatives, such as (±)-trichodiene, (±)-12,13-epoxytrichothec-9-ene, and (±)-trichodermol.[145,146]

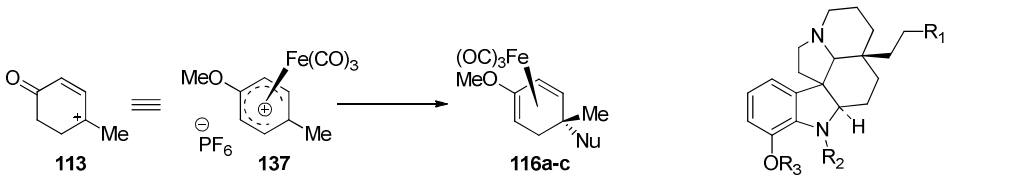
A similar strategy was applied to syntheses of the aphidicolin, stemodinane and related derivatives.[147,148]



Scheme 32 Synthesis of aphidicolin and trichtocene derivative.

2.3 Reactivity of Irontricarbonyl Cyclohexadienone Complexes

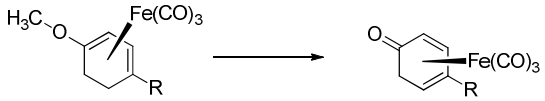
Cyclohexadienyl complexes show considerable promise as synthetic intermediates for organic synthesis. The cationic forms of methoxysubstituted complexes react with nucleophiles at the *para*-position. A cyclohexadienone coordinated to the iron tricarbonyl moiety is stable and tautomerization to phenol or Diels-Alder addition are not possible, in contrast to the uncomplexed form. These complexes react with a limited number of nucleophiles. This cyclohexenone γ-cation equivalent has been used in the synthesis of natural products including alkaloids (±)-limaspermine **139** and (±)-aspidospermine **138**.[149]



Scheme 33 Cyclohexadienyl complex as a γ-cyclohexanone as an intermediate to the alkaloids aspidospermine and limaspermine.

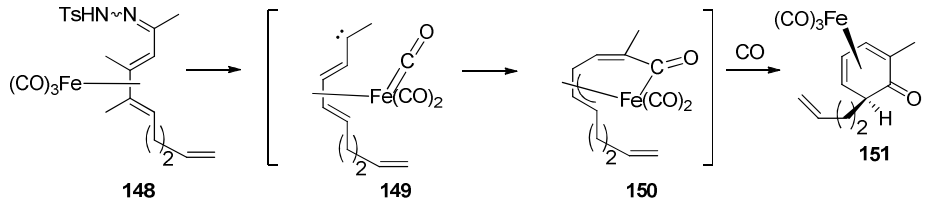
The most common method of decomplaxation of the $Fe(CO)_3$ fragment from the diene ligand is by oxidation. Hovewer, there are rare examples of oxidation of the diene ligand without decomplexation, e.g. to access cyclohexadienones.

Reboul *et al* have reported[150] preparation of novel 4-substituted-tricarbonyl(η^4-cyclohexa-2,4-dien-1-one)iron complexes **144-147** in moderate yields (12%-60%) (from 1-substituted-tricarbonyl(η^4-4-methoxy-cyclohexa-1,3-diene)iron complex **140-143** using thallium(III) trifluoroacetate or nitrate in methanol, or ethanol as depicted in Scheme **34**.



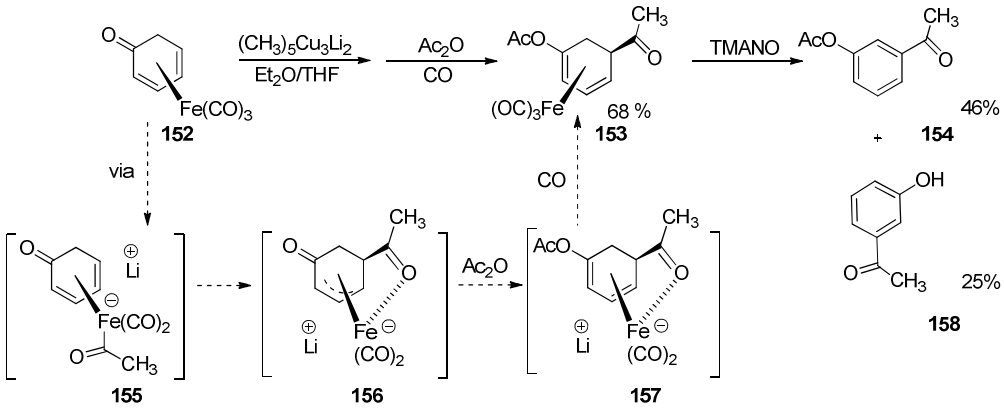
Scheme 34 Cyclohexadienyl complexes as a γ-cyclohexanone.
Reagents and conditions: $Tl(CF_3CO_2)_3$, EtOH, MeOH, 10 min, −10 ℃.

When acyclic tosylhydrazones of tricarbonyliron complexes fragment at high temperature (Bamford-Stevens type reaction), cyclohexa-2,4-dienones are obtained.[151]



Scheme 35 Preparation of cyclohexadienone from acyclic tosylhydrazone. Reagents and conditions: NaH, mesitylene, CO, 20 ℃ to 110 ℃, 20 min.

Interestingly, Narasaka *et al* have developed a method for the regioselective formation of *meta*-acyl phenols by reaction of alkyl cuprates and organoiron tricarbonyl complex **152** followed by treatment with acetic anhydride and carbon monoxide.[152]



Scheme 36 Reaction of cyclohexadienone iron complexes **152** with higher order methyl cuprate.

The removal of the iron scaffold was accomplished at room temperature with TMANO in *N*,*N*-dimethylacetamide for 1 h.

One year later, the same authors have employed (in a similar manner) iron tricarbonyl oximes and higher order cuprates followed by treatment with acetic anhydride and carbon monoxide leading to *m*-acylaniline derivatives in good yields after demetallation by oxidation with cerium(IV) ammonium nitrate.[153] Also, preparation of *m*-butylphenyl methyl ketones has been reported by this pathway.[154]

1-Substituted complexes are accessible by modification of an original procedure described by Birch, later developed by Stephenson *et al*.[155] They have demonstrated a powerful method of changing phenyl regiocontrol preference to the far end of (π)–system (C-5) by the use of the methoxy group at C-4 directing to the C-1 position at the η^4-cyclohexadiene.

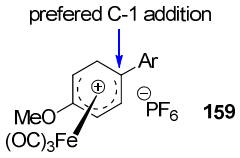
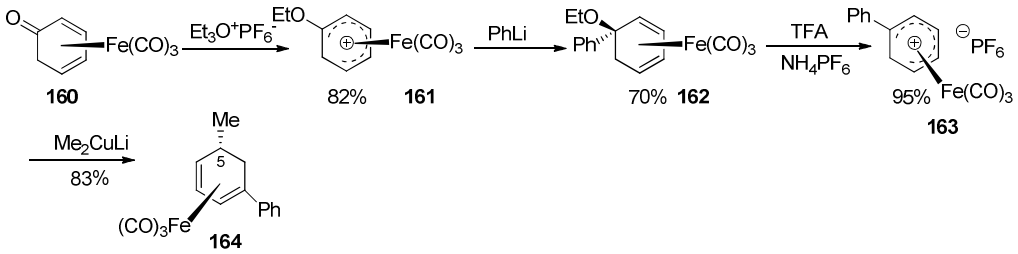


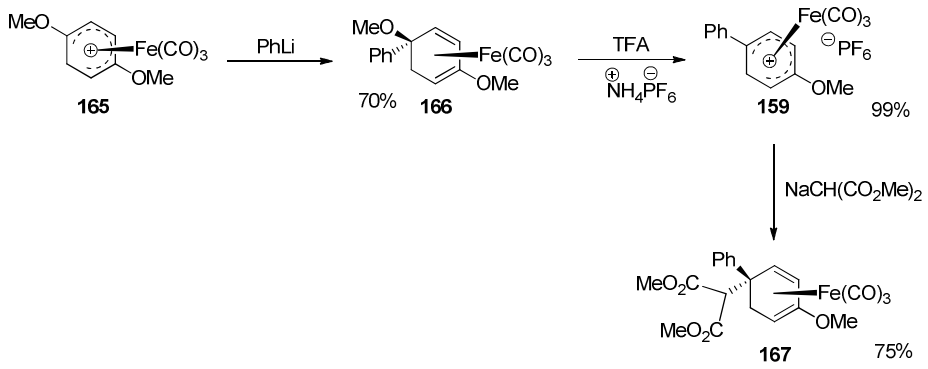
Figure 7 Demonstration of change of regioselectivity of methoxyl- and phenyl groups of η^4-cyclohexadiene complexes.

This novel approach is mediated by two nucleophilic additions with the *anti* stereochemistry to the metal as demonstrated in Scheme **37**.



Scheme 37 Demonstration of regioselectivity of alkoxy- and phenyl groups of η^4-cyclohexadiene complexes.

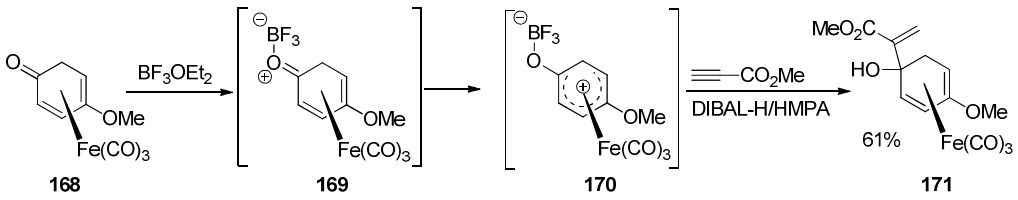
Anson *et al.* have demonstrated multiple use of iron tricarbonyl moiety as directing group to complete synthesis of highly enatiopure product (“auxiliary ligand”).[156] Scheme **38**



Scheme 38 Demonstration of regiodirecting effects of phenyl and methoxy groups of η^4-cyclohexadiene complexes.

Hudson *et al.* have reported the combination of hydroalumination/BF_3 activation as a practical method for elaboration of irontricarbonyl cyclohexadienone complexes.[157]

Hydroalumination of propargyl esters provided an organoaluminium nucleophile which upon direct treatment with dienone **168**, gave only starting material. Tsuda *et al.*[158] employed Lewis acid to enhance the electrophilicity, and the reaction with an excess of boron trifluoride etherate was employed, giving the C-C bond formation successfully **171** in 61% yield. It was also possible to convert product **171** further into a cationic η^5 intermediate, after acidic removal of the hydroxyl group.



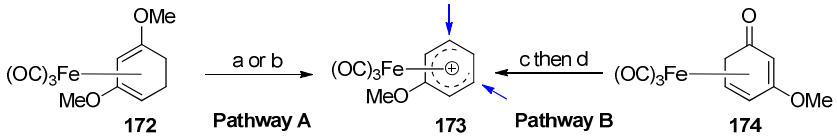
Scheme 39 Activation of cyclohexadienone iron complex with boron trifluoride etherate.

2.4 Regiochemistry

The substituted cationic (η^5-cyclohexadiene)iron complexe undergoes reactions with a wide range of anions, and the outcome of the reaction depends on the nature of the substituents. For instance with 1-CO_2Me or 2-OMe monosubstituted (η^5)-salts the nucleophilic attack occurs preferentially at the C-5 position (Scheme **26**, Entry **2,** Scheme **28** and **31**), except when very reactive anions are used.[116] Nevertheless, a weakly deactivating 2-Me group directs exclusively to C-5. (Scheme **26**, Entry **4**)

The preparation of 2-OMe cation **84** proceeds directly from the corresponding 2-OMe neutral complex, by hydride abstraction process. To access 1-OMe and 3-OMe salts the reaction is not straightforward as previously mentioned, because (η^5)-1-OMe is not stable in water during isolation and yields cyclohexadienone complex.[159,160]

Desired 3-OMe cationic product **173** can be accessed by treatment of **172** with strong acids (**Pathway A**) by OMe loss or from the cyclohexadienone **174**, $NaBH_4$ reduction followed by hexafluorophosphoric acid as an alternative **pathway B** as shown in Scheme **40**.



Scheme 40 Preparation of the 3-OMe cationic product.

Reagents and Conditions: (a) H_2SO_4, (80%); (b) trifluoroacetic acid at 0 ℃ (100%); (c) $NaBH_4$, dry 1,2-dimethoxyethane, 0 ℃, 12 h, isolation th en propionic anhydride HPF_6 aq., 15 min, 39%.

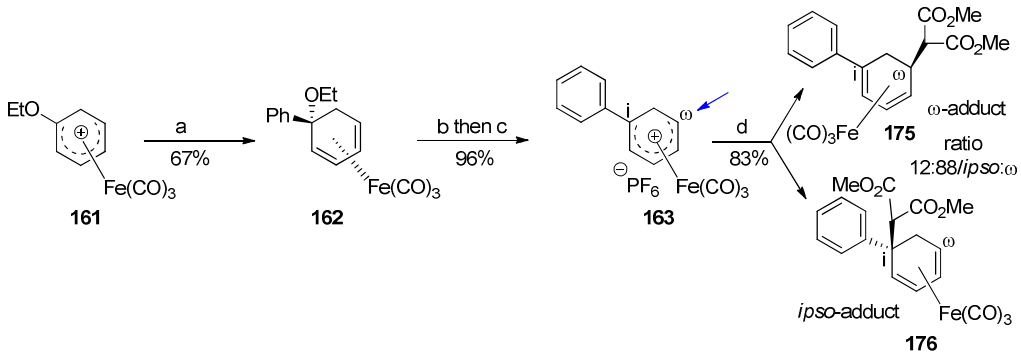
Directing effects are not a concern for the 3-OMe cation **173** due to its symmetrical nature.[159,114,161]

2.5 ARYL CYCLOHEXADIENE REACTIVITY

The cyclohexadiene ligand structure has been the most studied and was first prepared by Fischer in 1960. As described above, the reactivity of the corresponding stabilized cyclic η^5 cations with nucleophiles is wide in scope, including electron rich aromatic rings creating a new carbon-carbon bond.

There has been extensive research done employing 1-CO_2Me and 2-OMe groups in electrophilic cyclic iron complexes to direct substitution with a representative range of nucleophiles into to the distal end of the π-system (ω-directing). However, only a few research groups explored the formation and reactivity of *aryl* substituted electrophiles.[162,163,164,165,127,]

Monosubstituted 1-aryl cyclohexadienyl iron complex **163** was prepared from the 1-OEt corresponding complex **161** by treatment with phenyllithium, to give unstable intermediate **162** which upon treatment with acid and precipitation with NH_4PF_6 furnished **163** in 96% yield. The 1-Ar and 2-Ar monosubstituted products have shown strong ω-directing effects with a series of nucleophiles ($NaCH(CO_2Me)_2$, $NaBH_4$, Me_2CuLi).[163] However, the *ipso* position was accessible with more electrophilic Ar examples (4'-CF_3) and with stabilized enolates as nucleophiles.



Scheme 41 Preparation of 1-Phenyl cationic product **163** followed by nucleophilic addition. Reagents and Conditions: (a) PhLi, DCM, rt, 15-30 min, (67%); (b) trifluoroacetic acid; (c) NH_4PF_6; (d) $CH_2(CO_2Me)_2$/NaH.

Some groups in substituent cyclohexadienyl complexes direct to the same diene terminus ("mutually reinforcing effect") as shown in Figure **8**.

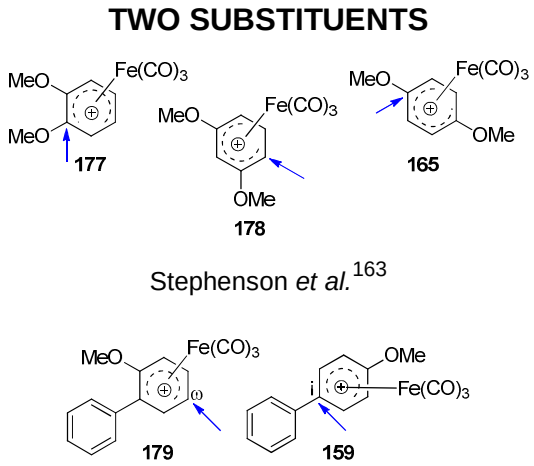


Figure 8 Some examples of the "mutually reinforcing effect".

As can be seen from the previous examples, cationic cyclohexadienyl complexes are very reactive towards nucleophilic additions, and these reactions are usually chemoselective, (the CO ligand typically does not undergo nucleophilic addition), highly regioselective (for complexes substituted with an EWG, cyclohexadienyl addition occurs into the ω position), and stereoselective (typically *anti*-addition to the metal).

Many monosubstituted cyclohexadienyl ligands are available, bearing at C1 electron donating or electron withdrawing groups. Directing effect of the 2-OMe group forces nucleophiles to attack into the ω-position (C-5) at the terminus of the diene system. The situation is more complicated for an ethoxy group which directs into the *ipso* position due to charge/orbital control.[166] Figure **9**

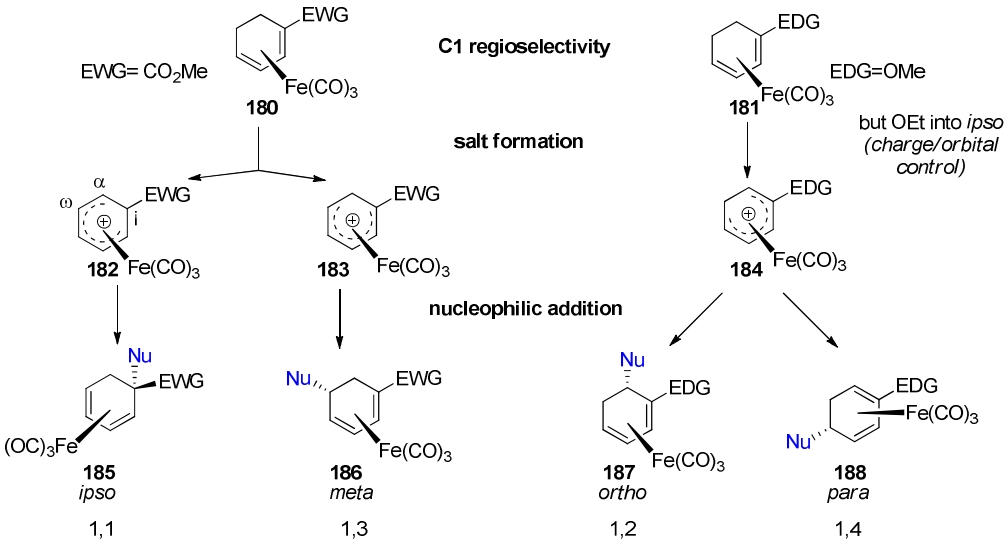
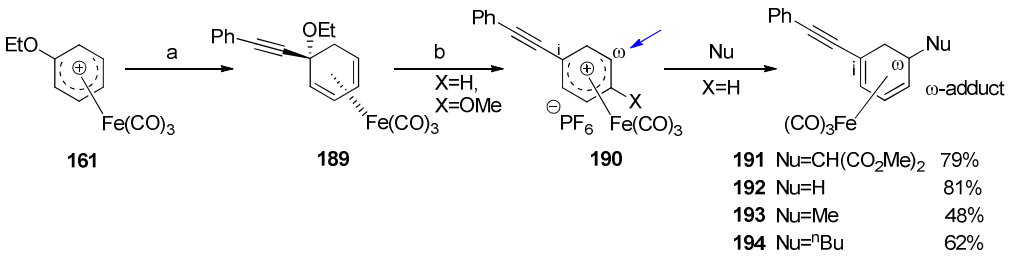


Figure 9 Directing effect of C1-substituted cyclohexadienyl cations.

2.6 The reactivity of 1-ethoxycyclohexadienyl salt

In 1997, Stephenson and co-workers reported[167] for the first time the preparation of alkyne-substituted tricarbonyl complex **190** and its reactivity. The methodology they used employed 1-ethoxycyclohexadienyl complex **161** and the aryl lithium reagent which attacks the *ipso* position as demonstrated in Scheme **42**.

A series of nucleophiles were tested for addition to alkynyl cyclohexadienol cation **190** and surprisingly the reaction is highly regioselective to give ω-addition products in good yields. The same regioselectivity (ω) is observed with electron withdrawing groups like CO_2Me and CN, but in the PhC≡C case the outcome depends on steric effects rather than electronic ones. The conclusion can be drawn that the alkyne substituent is a weaker ω directing group than CN.[167]



161 **189** **190**

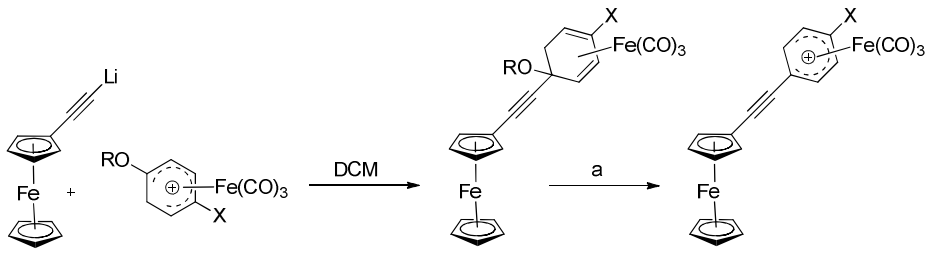
191 Nu=CH(CO_2Me)$_2$ 79%
192 Nu=H 81%
193 Nu=Me 48%
194 Nu=^{n}Bu 62%

Scheme 42 Preparation of 1-alkynyl substituted tricarbonyl(cyclohexadienyl)iron complex **190** followed by nucleophilic addition reactions.

Reagents and Conditions: (a) PhC≡CLi, (67%); (b) HPF_6, acetic anhydride, 70%; (c) $NaCH(CO_2Me)_2$, THF, 0 ℃, 79%; $NaBH_4$, CH_3CN, 0 ℃, 81%; Me_2CuLi, THF, 0 ℃, 48%; ^{n}BuLi, THF, 0 ℃, 62%; KCN(aq.) CH_3CN/H_2O -two products.

Ferrocenes have been extensively investigated as organometallic donors in donor-*π*-acceptor second order NLO chromophores. Hendrix *et al.*[168] for the first time investigated cationic η^5-cyclohexadiene iron complex **196** with dipolar structures to give a bimetallic monocation iron complex with a single alkyne spacer.

Irontricarbonyl(η^5-1-ethoxydienyl) complex reacted with lithiated acetylene **195** to give **196** in 79% yield. The product was subsequently treated with hexafluorophosphoric acid to afford cationic salt (η^5)-ferrocenylethyne-substituted cyclohexadienyl complex **198** in 71% yield. The same reaction sequence was repeated for 1,4-dimethoxy-substituted elecrophile **123**, but yields were lower.[168] Scheme **43**

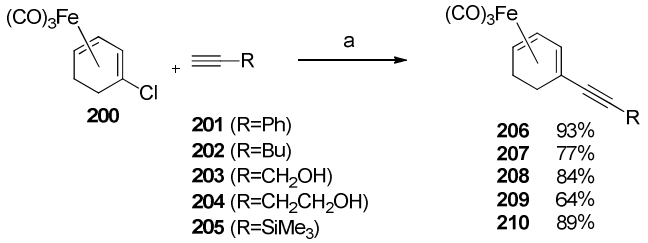


195 **161** R=Et; X=H, **123** R=Me; X=OMe **196** R=Et; X=H, 79% **197** R=Me; X=OMe 38% **198** R=Et; X=H, 71% **199** R=Me; X=OMe 58%

Scheme 43 Preparation of the bimetallic monocation iron complexes with a single alkyne spacer.

Reagents and Conditions: (a) HPF_6.

Significant result has been reported in the field of cross-coupling: (η^4-chlorodiene)$FeCO_3$ cyclohexadiene complex **200** underwent smooth coupling with terminal alkynes with 5 mol% of $PdCl_2(PPh_3)$/CuI at 60 ℃ in high yields. Complexation with the $Fe(CO)_3$ moiety clearly activates the vinylic C-Cl bond toward Pd(0) insertion allowing Sonogashira coupling (and also Heck coupling) to proceed smoothly under mild conditions.[169] Vinyl chlorides are generally unreactive in such cross-coupling processes.



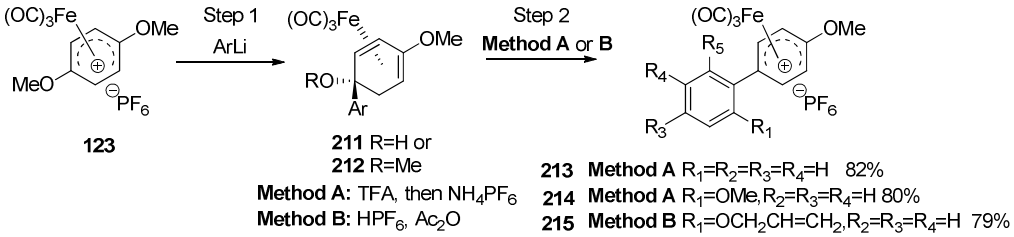
Scheme 44 The Sonogashira coupling of complex **200.**

Reagents and Conditions: (a) $PdCl_2(PPh_3)_2$ 5 mol%, CuI (5 mol%), Et_3N, 60 ℃, 3 h.

2.7 APPLICATIONS IN NATURAL PRODUCT SYNTHESIS

2.7.1 Natural products from the arylcyclohexadienyliron precursors

The use of organoiron electrophiles with mutually reinforcing groups is well understood.[163,170,171] Aryl substituents on tricarbonyl(cyclohexadienyl)iron complexes usually direct nucleophiles to the ω-position. However when the effect of an alkoxy substituent reinforces that of an arene substituent, there is a stronger directing effect favouring *ipso* addition of nucleophiles ω- to the arene and proximal to the alkoxy group.[172] The combination of a C(1)-OMe with the ω-directing group ensures nucleophile addition at C1 of η^5-cationic complex **123**.[165] Subsequent treatment with an acid[173], such as TFA or HPF_6, induces the methoxy group to leave, regenerating a "η^5-aryl salt". Scheme **45**



Scheme 45 Preparation of (1-arylcyclohexadienyl)iron complexes.

Stephenson *et al.* described a unified strategy to access both 1- and 2-arylcyclohexadienyl iron complexes.[165] When two sequential nucleophilic attacks take place at the same carbon atom (*ipso* to the aryl group) the strategy is referred to as a "*1*,*1*-strategy", giving a product with one quaternary centre.[165,174] When the addition take place at adjacent positions, two stereogenic quaternary centres are formed ("*1*,*2*-strategy").[165,171] This methodology offers access to a "C_{12}-building block strategy" for the synthesis of alkaloids such as mesembrine[175], *O*-methyljoubertiamine[171], hippeastrine[127], martidine[174,176] and lycorine[125], as well as various flavonoids[177]. Interestingly, highly substituted organic natural products *i.e.* lycoramine[174,178,179] could also be accessed by a related "C_{13}-central building block strategy"[165].

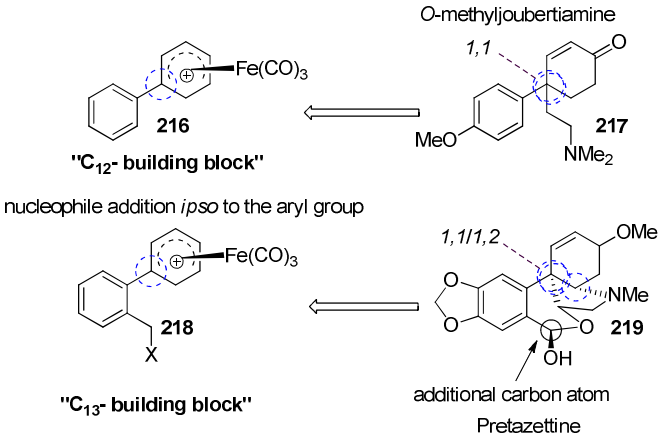
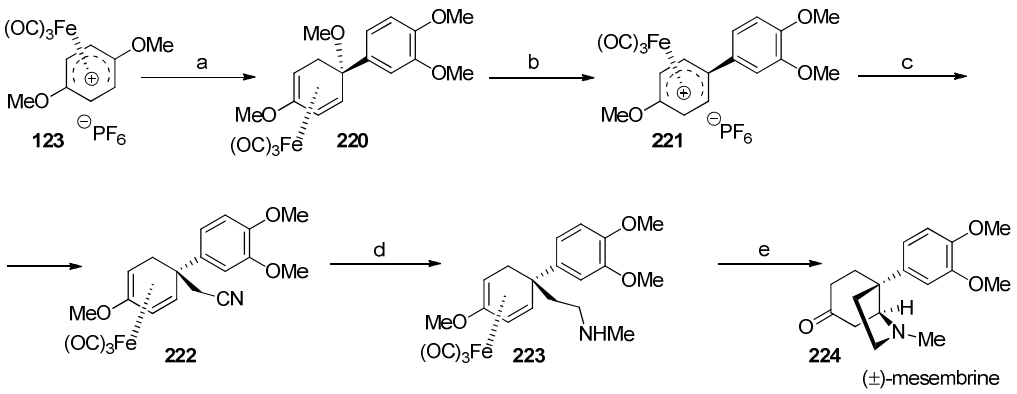


Figure 10 Example of a retrosynthetic analysis for *O*-methyljoubertiamine using the *1,1* pattern and for pretazettine using both the *1*,*1* and *1*,*2* patterns.

The *Sceletium* alkaloid (±)-mesembrine is a serotonin uptake inhibitor, and was prepared from **221** in just four steps by aforementioned "C_{12}-building block strategy".[175] To establish a quaternary centre through C-C bond formation 3,4-dimethoxyphenyllithium was employed as a nucleophile to react with prochiral tricarbonyl-(η^4-1,4-dimethoxycyclohexadiene)iron(0) to give **220** in 66% yield. Subsequently, acid mediated transformation gave η^5 salt **221** in over 80% yield. After generation of an enolate from 2-trimethylsilylethyl cyanoethanoate, and reaction with **221**, the reaction was quenched with TBAF, and heated at reflux for 3 h giving **222** in 77% yield in the one pot reaction.



Scheme 46 Preparation of (±)-mesembrine.

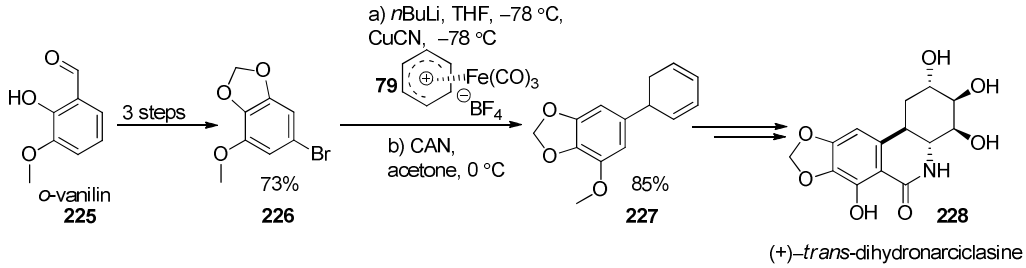
Reagents and Conditions: (a) $(3,4\text{-OMe})_2C_6H_3Li$, DCM, ether, −78 °C, 2.5 h, 66%; (b) 1. HPF_6 aq., Ac_2O, 2. NH_4PF_6 aq., 0 °C, rt., 30 min, 83%; (c) Na($Me_3SiCH_2CH_2O_2CCHCN$), THF, 0 °C, 1 h, then TBAF, THF, reflux, 3 h, 77%; (d) DIBAL-H, DCM, −78 °C, 2 h then 0 °C, 1 h, then NH_4Br in MeOH, then $MeNH_2$ in MeOH, $NaBH_4$ in MeOH, rt., 2 h, then aq HCl, then NaOH, 79%; (e) Me_3NO, acetone, rt, 16 h, then $(CO_2H)_2 \cdot 2H_2O$, MeOH, rt., 3 h, then NaOH aq. 20 min, 52%.

Reduction with DIBAL-H, and addition of ammonium bromide and methyl amine in methanol followed by sodium borohydride delivered secondary amine **223** by reductive amination in 79% yield.

Demetallation was accomplished with TMANO in acetone followed by quenching with oxalic acid, and simple work up furnished target product **224** (±)-mesembrine in 52% yield.[175] Using the same methodology, the same authors

have also reported a new class of tricyclic η^4-dieneiron complexes possessing a fused cyclopentane ring system.[180]

Biologically active natural products of the *Amaryllidaceae* group show potent antitumor and antiviral activity. In 2008, Studer *et al.* reported[181] the first total synthesis of one natural product of this class, *trans*-dihydronarciclasine **228** which has shown activity against selected human cancer cell lines. The synthesis was accomplished in 17 steps, starting from commercially available *o*-vanilin **225** in 5.6% overall yield. A key step of the synthesis was a *nitroso*-Diels–Alder reaction.[181] (Scheme **47**)



Scheme 47 Synthesis of (+)−*trans*-dihydronarciclasine.
Reagents and Conditions: (a) *n*BuLi, THF, −78 °C; (b) CAN, acetone, 0 °C.

In 2010, Stephenson and co-workers extended this methodology, employing irontricarbonyl diene complexes, in a novel tandem decomplexation-nitroso Diels–Alder (NDA) reaction. The resultant cycloadducts are formed with correct regioselectivity for application in an organoiron-mediated synthesis of the alkaloid hippeastrine.[182]

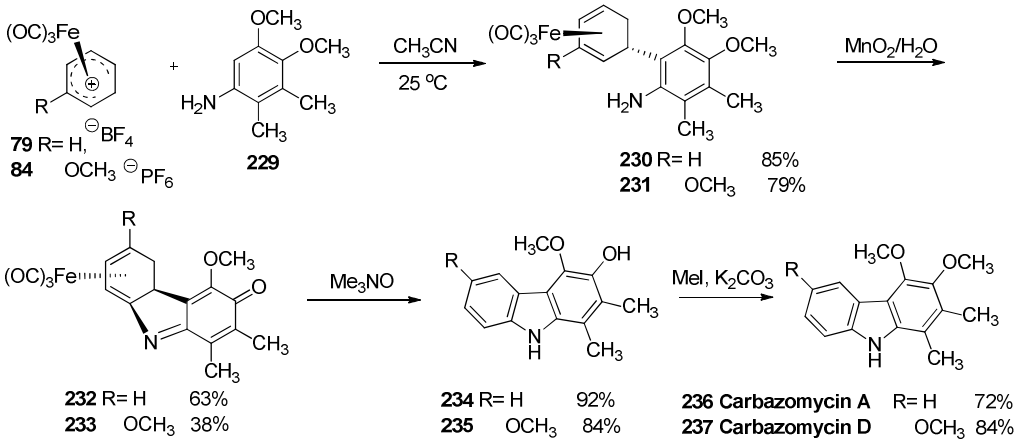
2.7.2 CARBAZOLES

In 1959 Schmutz *et al*. were the first to describe[183] a naturally occurring carbazole olivacine, which was isolated from *Aspidosperma olivaceum*. Later,

from a small Indian tree -*Murraya koenigii*, commonly known as the curry-leaf tree, isolation of another novel carbazole alkaloid was reported and named murrayanine.[184]

Carbazomycins belong to a group of rare microbial quinone antibiotics which contain a carbazole nucleus and represent a novel class of antifungal, antimicrobial and also potential anti-tuberculosis drug candidates.[185,186]

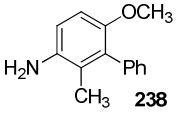
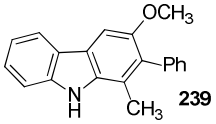
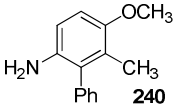
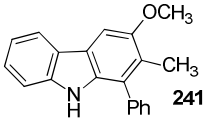
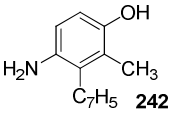
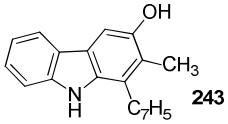
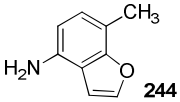
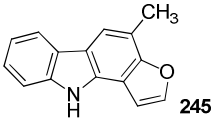
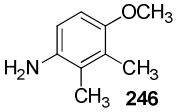
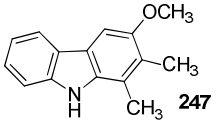
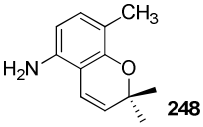
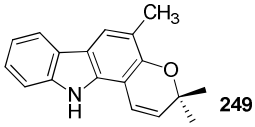
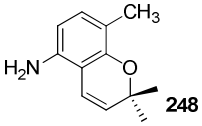
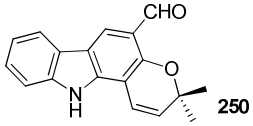
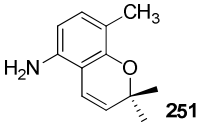
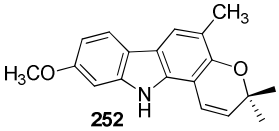
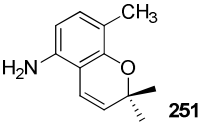
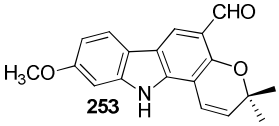
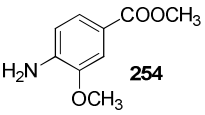
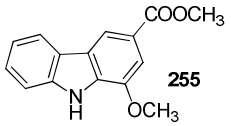
An iron mediated carbazole synthesis may be achieved by C-C bond formation between the aryl amine **229** with iron tricarbonyl cation **79** (or its methoxy analogue **84**) which proceeds via electrophilic substitution, and then C-N bond formation is accomplished by an oxidative cyclization with manganese dioxide, followed by demetallation with TMANO and methylation to provide Carbazomycin A, and Carbazomycin D.[187,188]

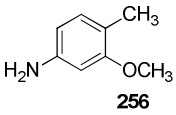
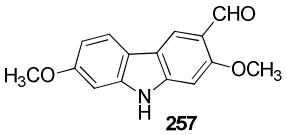
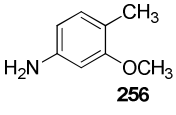
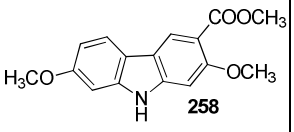
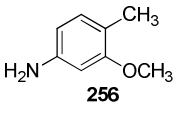
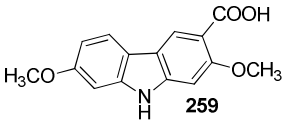
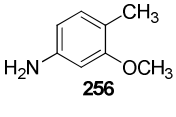
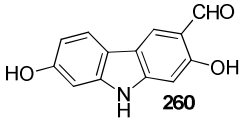
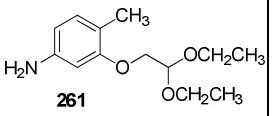
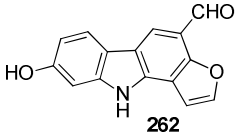
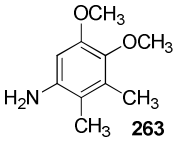
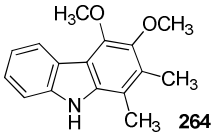
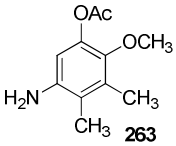
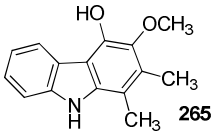
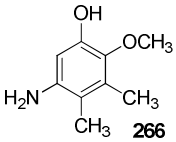
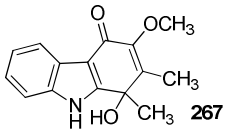
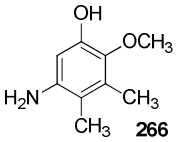
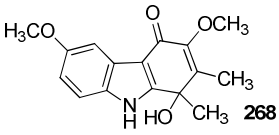
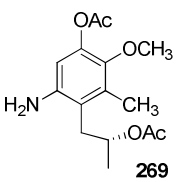
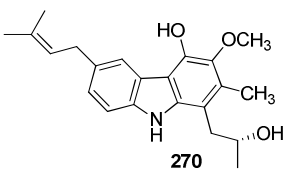


Scheme 48 Synthesis of Carbazomycin A and D.

Starting from the appropriate aryl amine, a similar sequence of events provided access to a wide range of carbazoles. (Table **2**)

Table 2 Iron mediated synthesis of carbazoles. "-" yield not reported although product was obtained.

cation	aromatic amine	product	Name	Overall yield
79	 **238**	 **239**	isohyellazole	73%[189]
79	 **240**	 **241**	hyellazole	88%[189]
79	 **242**	 **243**	carazostatin	45%[190]
79	 **244**	 **245**	furostifoline	21%[191]
79	 **246**	 **247**	4-deoxy carbazomycin B	49%[192]
79	 **248**	 **249**	girinimbine	58%[193]
79	 **248**	 **250**	murrayacine	59%[193]
84	 **251**	 **252**	*O*-methyl murrayamine A	59%[193]
84	 **251**	 **253**	7-methoxy murrayacine	55%[193]
84	 **254**	 **255**	mukonine[194]	33%

84	 **256**	 **257**	7-methoxy-*O*-methylmukonal [195]	-
84	 **256**	 **258**	clausine H (clauszoline-C) [195]	-
84	 **256**	 **259**	clausine K (clauszoline-J)	18% [195]
84	 **256**	 **260**	clausine O [195]	-
84	 **261**	 **262**	furoclausine-A	9% [196]
84	 **263**	 **264**	carbazomycin A	65% [187]
84	 **263**	 **265**	carbazomycin B	55% [187]
84	 **266**	 **267**	carbazomycin G	46% [197]
84	 **266**	 **268**	carbazomycin H	7% [197]
79	 **269**	 **270**	neocarazostatin B	36% [198]

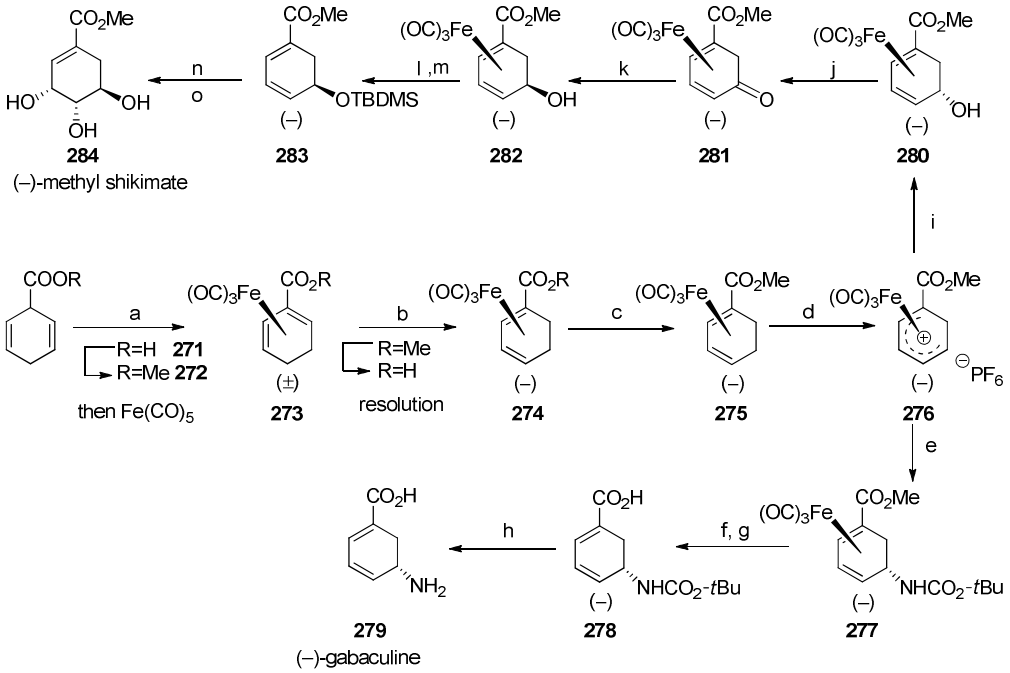
Several further applications of the iron-mediated methodology were applied in the synthesis of carbazole alkaloids, Hyellazole and 6-chlorohyellazole,[199] murrayanine, koenoline, murrayafoline A[200], anhydrolycorinone, hippadine[201], discorhabdin and prianosin alkaloids.[202]

2.7.3 GABACULINE

Birch *et al.* employed[203] cyclohexadiene-tricarbonyliron complex **276** to prepare (-)-gabaculine **279** a naturally occurring amino acid, which is a potent inhibitor of GABA-T catabolising enzyme. Gabaculine could potentially be useful for the treatment of Parkinsons, epilepsy and schizophrenia, because inhibition of 4-aminobutyrate:2-oxo-glutarate animotransferase increases the level of gamma-aminobutyric acid (GABA) in the brain.

Birch reduction of methyl benzoate followed by complexation of **272** under thermal conditions with iron pentacarbonyl provided (±)−2-carbomethoxycyclohexadiene-$Fe(CO)_3$ complex **273**. (Scheme **49**)

Isomerisation was carried out in methanolic sulphuric acid at reflux over 24h, leading to **274** in 90-95% yield. Complex **274** was resolved through the 1-phenylethyl ammonium salt, and after several recrystallisations followed by acidic hydrolysis provided pure (−)-acid **274**. This was subjected to methylation with diazomethane leading to corresponding ester **275** in quantitative yield. To a solution of trityl hexafluorophosphate in DCM was added **275** in hexane and after standing for 3 h, an orange precipitate was collected and purified by precipitation with ether of an acetone solution to give **276** in 73% yield.



Scheme 49 Syntheses of (−)-gabaculine and (−)-methyl shikimate.

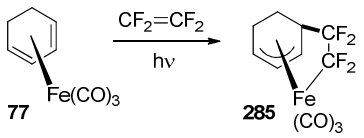
Reagents and conditions: (a) KOH, dimethyl sulphate, 30 min at rt.→reflux for 5 h, then $Fe(CO)_5$, heat; (b) sulfuric acid, MeOH, reflux, 24 h, then H_2O, reflux, 30 h, 95%, then resolution with (−)-1-Phenylethylamine; (c) CH_2N_2, Et_2O, rt., 30 min, quantitative; (d) Ph_3CPF_6, DCM, 73%; (e) H_2NCO_2-*t*-Bu (2.2 equiv), Hünig's base, DCM, 0 ℃, 5 min, 81 %; (f) Me_3NO, CH_3CONMe_2, −15 °C, 3 h, then 0 °C, 16 h, 80%; (g) NaOH, MeOH, H_2O, 66% (h) 3 M HCl, MeOH, ion-exchange column; (i) $NaHCO_3$/aqueous CH_3CN, 95%; (j) CrO_3, pyridine, DCM, 85%; (k) $NaBH_4$, $ZnCl_2$, Et_2O, 98%; (l) TBDMS triflate, DMF, Hünig's base; 83%; (m) Me_3NO, benzene, 82%; (n) 1 equiv. OsO_4/acetone, 67%; (o) $(n\text{Bu})_4NF$/THF, 85%.

Nucleophilic addition of *tert*-butyl carbamate in DCM, in the presence of diisopropylamine delivered **277** in 81% yield after column chromatography on silica. Demetallation with TMANO overnight and subsequent hydrolysis of the crude diene ester with 2 M NaOH in methanol provided pure acid **278** which was isolated after recrystallization from hexane-ether in 66% yield. This underwent Boc deprotection hydrolysis in MeOH with 3 M HCl, leading to (−)-gabaculine **279** after purification on ion-exchange column.[203]

In addition, in 1988, the same authors reported a synthesis of the natural enantiomer of (−)-methyl shikimate **284**[204] starting from the same resolved iron cations **276** as depicted in Scheme **49**.[205]

2.8 SPIROCOMPOUNDS

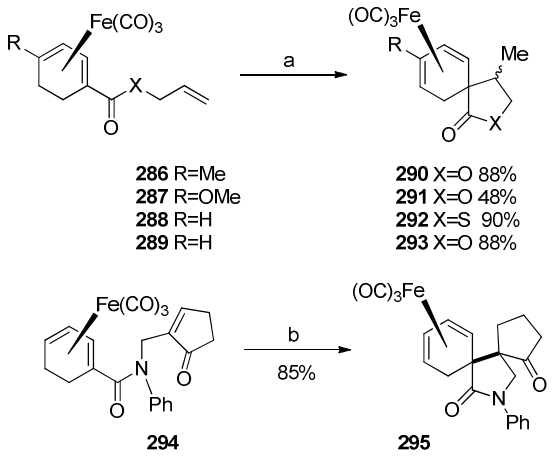
In 1975, Green and co-workers[206] reported a new reaction with tetrafluoroethylene in which iron complex **77** under U.V. irradiation affords a π-allyl product **285** where the new C-C bond is formed at the less substituted end of the diene.



Scheme 50 Reaction of cyclohexadiene with C_2F_4 under photochemical conditions.

This has led to the development of methods for intramolecular cyclocoupling reactions, suitable for the construction of quaternary centres through C-C bond formation.[207]

The most useful substrates are allylic amide derivatives which under thermal conditions generate spirocyclic products. Additional substituents on the pendant olefin have the effect of decreasing the yield, which is attributed to steric hindrance. Under photothermal conditions allylic ester and allylic thioester systems underwent cyclization.[208] (Scheme **51**)

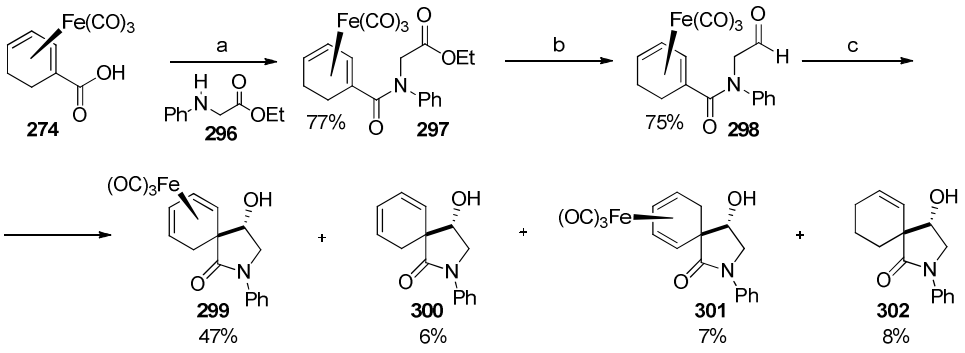


Scheme 51 Intramolecular coupling of olefin with diene-$Fe(CO)_3$ moiety.

Reagents and conditions: (a) *n*-Bu_2O, reflux, CO, 12 h; (b) *n*-Bu_2O, reflux, CO, 6.5 h, 85%.

The overall cyclization reactions of allylic thioester derivatives of cyclohexadiene iron tricarbonyl systems is similar to [6π+2π] ene reaction, leading to the formation of spiro thialactone derivatives.[208] This intramolecular iron tricarbonyl-promoted all-carbon [6+2] ene type spirocyclisation likely proceeds via a mechanism similar to the carbonyl-ene type of spirocyclisation.

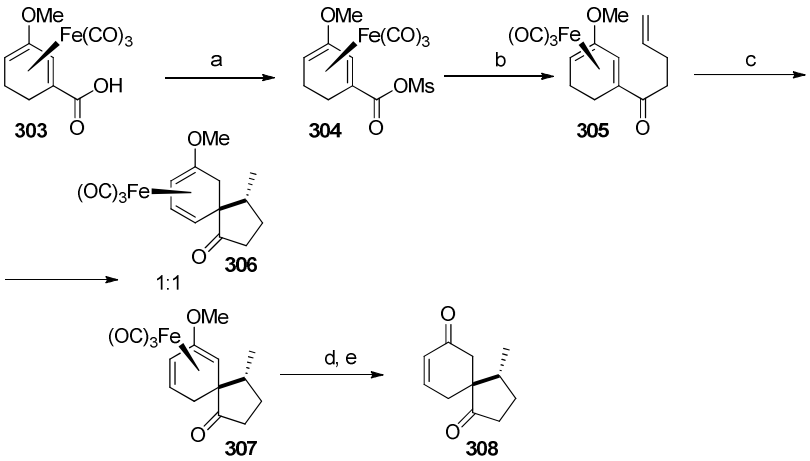
Pearson expanded the scope of this spirocyclisation reaction with a pendant carbonyl group promoted by iron to afford products with a functionalisable hydroxyl group at C4.[209] (Scheme **52**)



Scheme 52 Carbonyl-ene-type of spirocyclisation.

Reagents and conditions: (a) MsCl, DIEA, CH_2Cl_2, 0 ℃, 1 h, followed by ethyl 2-(phenylamino)acetate **296**, 24 h, 40 ℃, 77%; (b) DIBAL-H (1.5M in toluene), DCM, −78 ℃, 1 h, 75%; (c) toluene, 350 nm, 12 h, 100 ℃.

Introduction of a methoxy group at the C-3 position of the diene moiety controls pre- and postcyclization rearrangements of the diene $Fe(CO)_3$ unit.[210,211] (Scheme **53**)



Scheme 53 All-carbon cyclization via ketone intermediate.

Reagents and conditions: (a) MsCl, Et_3N, CH_2Cl_2, 0 ℃, 85%; (b) Et_2O, 3-butenylmagnesium bromide (0.67 mL, 1.1 M in Et_2O), 72%; (c) *n*-Bu_2O, CO, 5 h, 142 ℃, 90%, 1:1 mixture separated by preparative TLC purification (1:4/EtOAc:Hex); (d) Me_3NO (36.0 eq.), benzene, rt., 16 h, Ar; (e) MeOH, oxalic acid in water (15.5 eq.), rt., 12 h, 75%.

This chemistry can be applied to the total synthesis of 18-deoxycytochalasin H **309**, a natural product that is a potent HIV-1 protease inhibitor. A preliminary communication of part of this work has previously been published. [212,213] (Figure **11**)

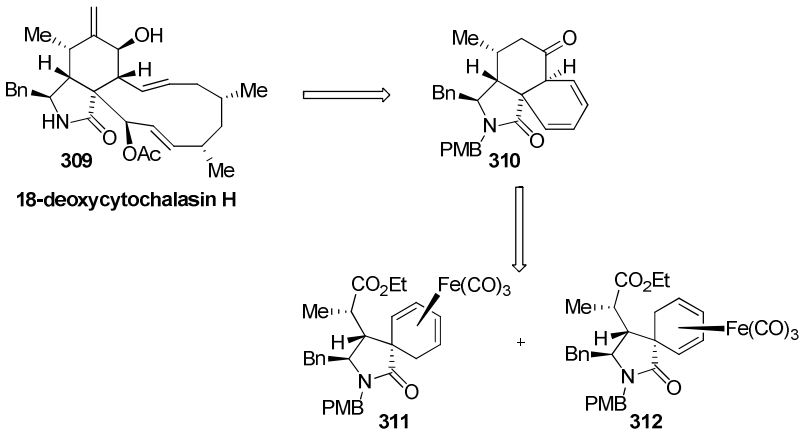
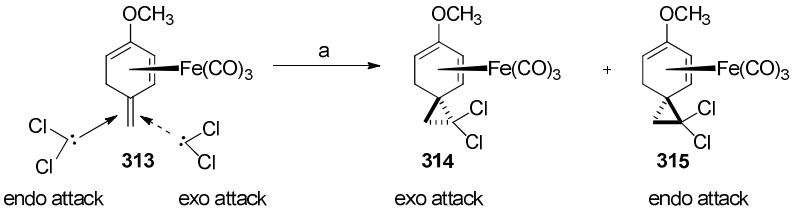


Figure 11 A Possible Approach to 18-Deoxycytochalasin H.

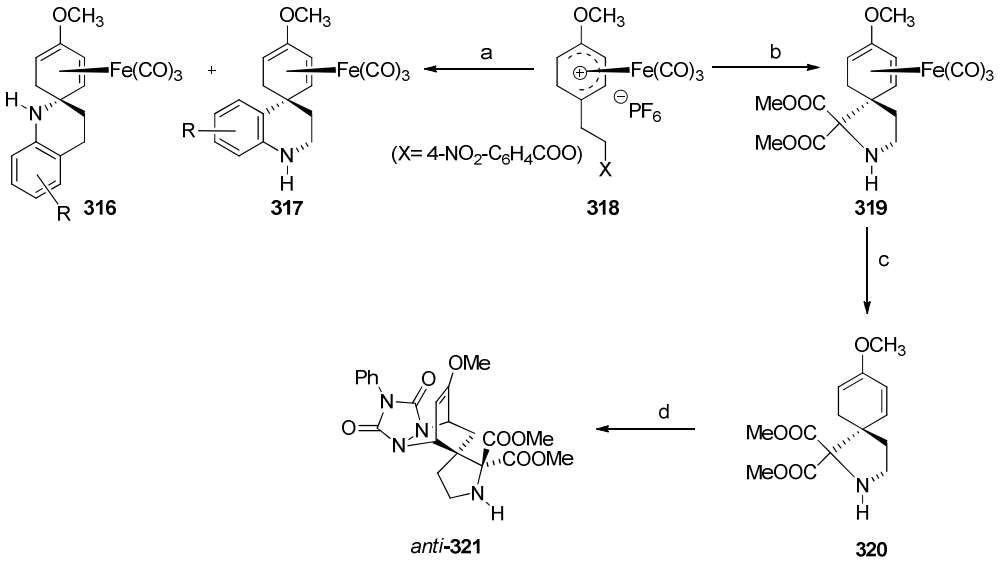
Ong *et al.* have reported a very useful (2+1) cycloaddition reaction between tricarbonyl[(1-4-*η*)-2-methoxy-5-methylene-cyclohexa-1,3-diene]iron **313** with a carbene for the rapid preparation of a spiro[2,5]octane system.[214] Interestingly, their first attempt with chlorocarbene did not undergo (2+1)cycloaddition, but dichlorocarbene gave a mixture of two diastereomers as a 9:1 mixture of **314** and **315**, estimated from the accurate integrated ^{1}H NMR spectra. Reaction with dibromocarbene provided a single diastereoisomer: the *endo* cyclopropanation did not occur, due to steric hindrance. As depicted in Scheme **54**.



Scheme 54 Possible approach of carbene to **313** from the *exo* and *endo* face.
Reagents and conditions: (a) $CHCl_3$, *t*-BuOK, pentane, 0 ℃.

Knölker *et al.* described a method of diastereoselective spiroannelation of arylamines with cationic cyclohexadiene salts which is dependent on the reaction temperature. Formation of **317** is favoured over **316** at low temperatures.[202] Dimethyl aminomalonate reacts with **318** overnight at room temperature to

deliver the tricarbonyliron-coordinated 2-azaspiro[4.5]decane **319** exclusively.[215] Demetallation of **319** with anhydrous TMANO in acetone at 23 ℃ was accomplished in 83% yield, and Diels-Alder reaction was attempted between iron free product and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). Scheme **55**



Scheme 55 Iron-mediated spiroannelation of arylamines and dimethyl aminomalonate followed by Diels-Alder reaction of the spirycyclohexa-1,3-diene **320**.

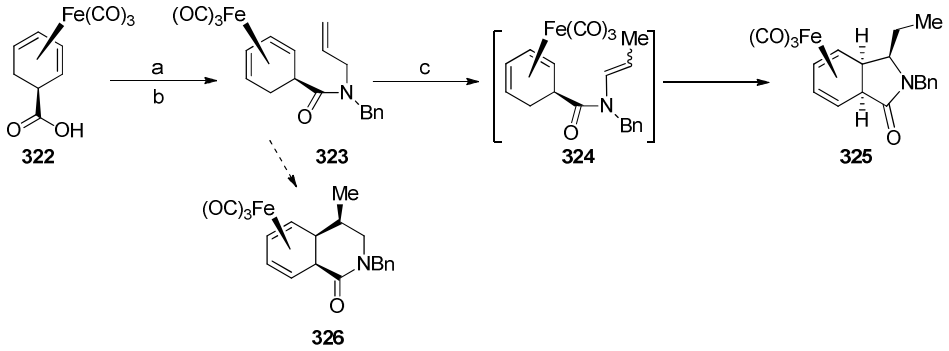
Reagents and conditions: (a) $ArNH_2$, MeCN, 82 ℃, 2 h (53–93%); (b) 2 equiv. of dimeth yl aminomalonate, MeCN, 25 ℃, 14 h (98%); (c) Me3NO, acetone, 25 ℃, 3h, (83%); (d) PTAD, CH2Cl2, −30 ℃ to −10 ℃, 1h, (68%);

2.9 Double Cyclization

2.9.1 Bicyclic Molecules by Rearrangement-Cyclization

The methodology described in Section **2.8** was extended to amides, in an attempted preparation of six-membered lactams. The synthesis began with amide complex **323**, which was prepared from acid **322** and *N*-benzylallyl amine. As previously mentioned, the cyclization reaction proceeds via coordination of

the pendant double bond to the iron moiety, which is in the *cis* stereochemistry. Scheme **56**.



Scheme 56 Iron-mediated [6+2]-ene-type cyclization.

Reagents and conditions: (a) $(COCl)_2$, pyridine, MS, CH_2Cl_2; (b) pyridine, *N*-benzylallylamine (90%); (c) *n*-Bu_2O, reflux, CO.

The same authors also reported a one pot cyclization to produce bicyclic architectures starting from 1,4-dihydrobenzoic acid, followed by amidation and complexation in the presence of $Fe(CO)_5$, under a CO atmosphere in refluxing di-*n*-butyl ether (0.02 mol/L). Compound **325** has a bicyclic framework and stereochemistry identical with a natural product gelsemine **327**, and this methodology is a promising approach to its derivatives.[216] (Figure **12**)

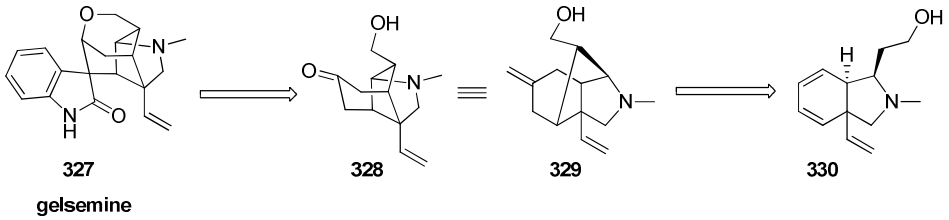
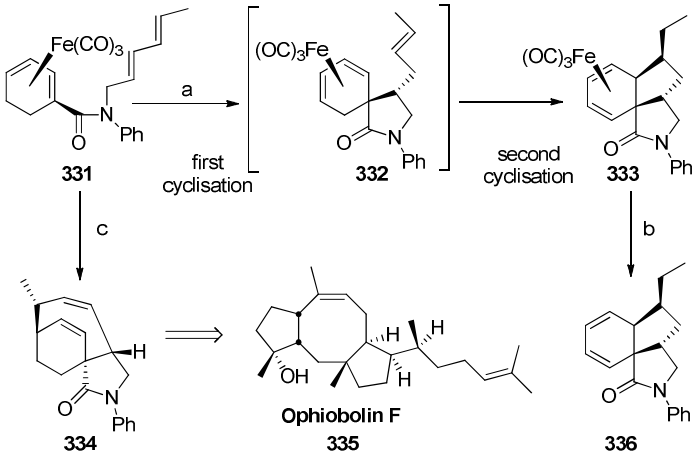


Figure 12 Retrosynthetic analysis of gelsemine.

If an appended 1,3-diene is used, a complex tricyclic molecule **333** can be obtained by tandem double cyclization.[216] (Scheme **57**).

Removal of the iron tricarbonyl scaffold leads to formation of tricyclic organic structures **336**. When **331** was treated with 2.2 equiv of TMANO added in four

portions at room temperature over 12 h, the cyclooctadiene **334** was formed as a single stereoisomer in quantitative yield.[217] This ring system is found in natural product structures such as ophiobolins C and F.



Scheme 57 Iron-mediated double cyclization of pendant dienes.
Reagents and conditions: (a) *n*-Bu_2O, 142 °C, CO; (b) Me_3NO; (c) 2.2 equiv Me_3NO in four portions, 12 h, CH_3CN, rt, quantitative.

2.10 TAMIFLU

Many records showed that human influenza and the avian flu (H5N1) have caused numerous deaths in many countries.[218,219] Oseltamivir phosphate is a potent neuraminidase inhibitor and the most widely used anti-influenza drug: only this drug was approved as an orally bioavailable drug for both treatment prophylaxis of flu.[220] Considering the worldwide demand for Tamiflu, improved production methods are needed.

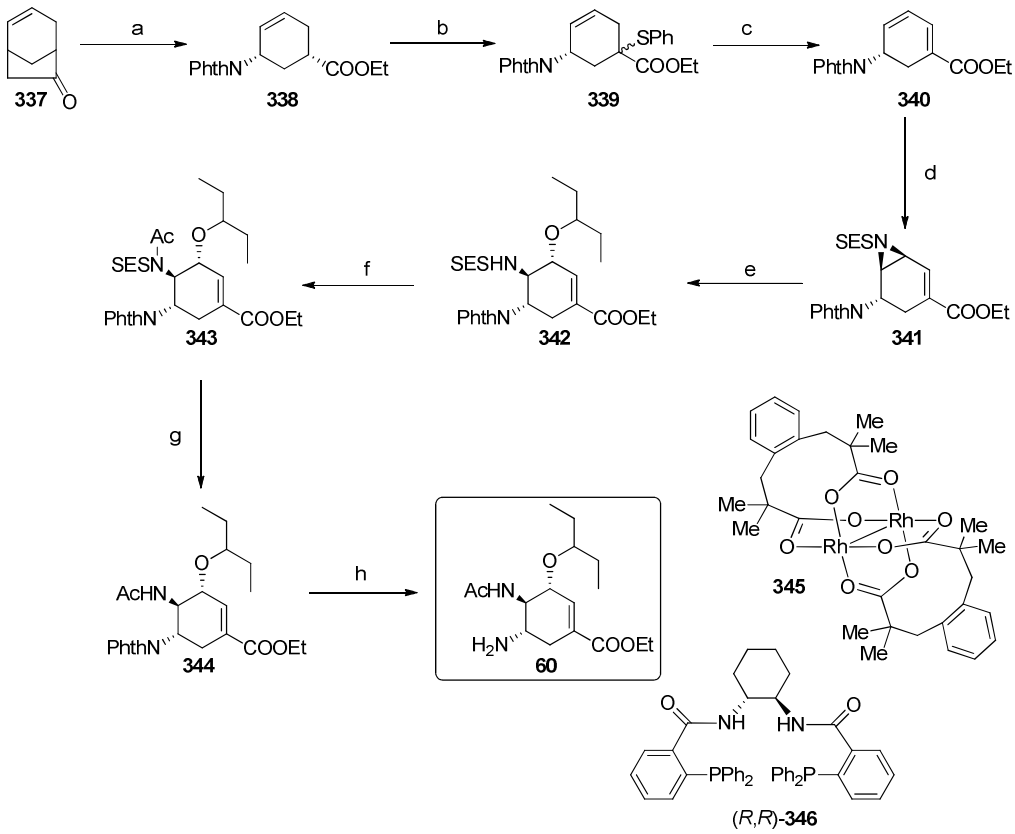
Nowadays, the procedure developed by F. Hoffman-La Roche, has been use commercially, utilising naturally occurring shikimic acid as a starting point, which is a limited resource subject to fluctuations in supply.[221,222]

In contrast to the current process route Corey's route using a catalytic asymmetric Diels-Alder reaction is very attractive because no expensive starting material and no hard-to-deal-with azide reagent were needed.[223]

In 2008, the shortest synthesis of (−)-oseltamivir **60** (8 steps from commercially available materials, overall yield 30%) was reported by Trost and co-workers.[224] (Scheme **58**)

Commercially available racemic lactone **337** was opened using [(η^3-$C_3H_5PdCl)_2$], and the Trost ligand (*R*,*R*)-**346** as the catalyst, and with TMS-phthalimide as a nucleophile to give TMS-caboxylate further converted *in situ* to **338** in 84% yield and 98% e.e in one pot. Treatment of **338** with fresh KHMDS in THF at −78 ℃ for 6 h, followed by $PhSSO_2Ph$ afforded an approximate 1:1 diasteromeric mixture of α-thioester **339** in 94% yield.

Oxidation of **339** with 70% *m*-CPBA in toluene formed the corresponding sulfoxide intermediate, which provided an elimination product **340** as 10:1 regioisomeric mixture after purification by silica gel column in 85% yield. The mixture was carried on into the next step of selective aziridination reaction with $PhI(OPiv)_2$ and $SESNH_2$, followed by the catalyst [$Rh_2(esp)_2$] and base MgO, the single product **341** was delivered in 86% yield after column chromatography (10:1 Petrol/EtOAc).



Scheme 58 Synthesis of (−)-oseltamivir by Torst *et al*.

Reagents and conditions: (a) 2.5 mol% [(η^3-$C_3H_5PdCl)_2$], 7.5 mol% (*R*,*R*)-**344**, trimethylsilylphthalimide (1.5 equiv.), THF, 40 ℃, then $TsOH \cdot H_2O$, EtOH, reflux, 84%, 98% e.e.; (b) KHMDS (1.5 equiv.), $PhSSO_2Ph$ (1.8 equiv.), THF, −78 °C to rt., 94%; (c) *m*-CPBA (1.0 equiv.), $NaHCO_3$ (2.0 equiv.), 0 ℃, then DBU (1.0 equiv.), 60 ℃, toluene, 85%; (d) 2 mol% **343**, $SESNH_2$ (1.1 equiv.), PHI-$(O_2CCMe_3)_2$ (1.3 equiv.), MgO (2.3 equiv.), PhCl, 0 ℃ to rt., 86%; (e) $BF_3 \cdot Et_2O$ (1.5 equiv.), 3-pentanol, 75 ℃, 65%; (f) DMAP (2 .0 equiv.), pyridine (20.0 equiv.), Ac_2O, MW, 150 ℃, 1 h, 84%; (g) TBAF (2.0 equiv.), THF , rt., 95%; (h) NH_2NH_2 (5.0 equiv.), EtOH, 68 ℃, quant.

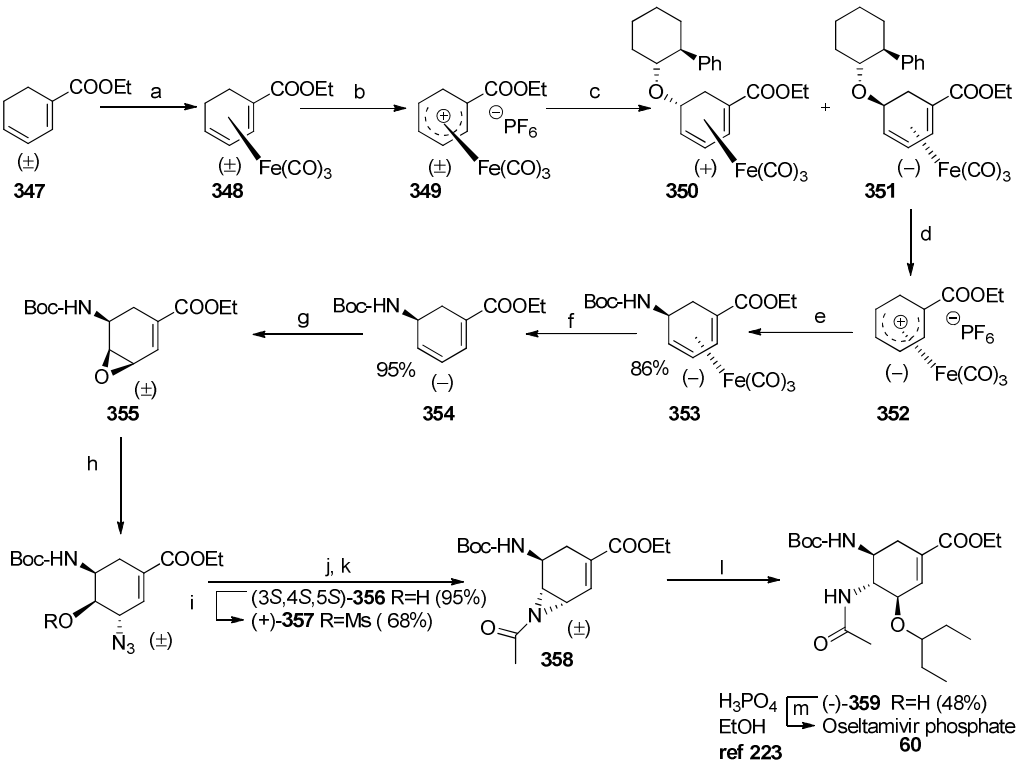
Then aziridine **341** was opened with $BF_3 \cdot Et_2O$ in 3-pentanol at 75 ℃ to afford **342** in 65% yield. Subsequent treatment of **342** with DMAP in Ac_2O and pyridine was subjected to microwave heating at 150 ℃ for 1 hr and after purification by column chromatography yielded **343** (84%). Removal of the SES protecting group was accomplished in 95% yield, after treatment of **343** with 1 M solution of

TBAF. Then after reaction of **344** with hot ethanolic hydrazine for 10 h delivered the final product (−)-oseltamivir **60** in quantitative yield.

The synthesis of oseltamivir phosphate based on cationic iron carbonyl chemistry was reported by Kann *et al.* in 2007.[225] (Scheme **59**)

The starting point of the synthesis was cyclohexadienoic acid ethyl ester **347** which was converted to (±)-iron tricarbonyl complex **348**, after treatment with diiron nonacarbonyl in toluene at 55 ℃ overnight, in 86% yield after column chromatography. A resolution was performed on corresponding cationic mixture of enantiomers **349** provided by hydride abstraction with trityl cation - after nucleophilic addition of (−)-(1*R*,2*S*)-*trans*-2-phenylcyclohexanol a mixture of separable diastereomers **350** and **351** were formed in 75% yield. Subsequent treatment with hexafluorophosphoric acid of both chiral ethers provided enantiopure salts (−)-**352** and (+)-**352** in high yield, which where then employed in a second nucleophilic addition with Boc-amine in the presence of Hünig's base, an approach which has some similarity with the procedure of the synthesis of (±)- and (−)-gabaculine reported by Birch *et al*.[203] The reaction was carried out with very slow addition of base, which improved the yield up to 86% for both products. Demetallation was achieved with hydrogen peroxide in aqueous sodium hydroxide to afford two enantiomers in 95% yield. Selective epoxidation of (−)-**354** with *m*-CPBA resulted in the formation of (+)-**355** also in 95% yield based on the crude, followed by ring opening with sodium azide to the corresponding azido alcohol **356** in 95% yield and then mesylation and purification to give (±)-**357** in 68% yield. Addition of triphenylphosphine followed by Et_3N into a solution of (±)-**357** in THF/H_2O at room temperature gave aziridine, which was then acetylated *in situ* leading to (±)-**358** in an overall yield of 65% after purification by column chromatography. The final stage of the synthesis of Tamiflu **60** was aziridine ring opening by treatment with $Cu(OTf)_2$ catalyst as depicted in Scheme **59**. This novel synthesis which utilized cationic iron intermediates was accomplished in a total 12 steps from cyclohexadienoic acid

ethyl ester (**347**). Final product **60** (Tamiflu) was formed after Boc group deprotection and salt formation with phosphoric acid in ethanol.



Scheme 59 Synthesis of (−)-oseltamivir by Kann *et al*.

Reagents and conditions: (a) $Fe_2(CO)_9$, toluene, 55 °C, 86%; (b) Ph_3CPF_6, DCM, rt., 94%; (c) Hünig's base, (−)-(1*R*,2*S*)-trans-2-phenylcyclohexanol, DCM, 0 °C, 5 min, 75%, HPLC separation; (d) HPF_6, Et_2O, 0 °C, 94%; (e) Boc-NH_2, Hünig's base, DCM, 0 °C, 86%; (f) H_2O_2, NaOH, EtOH, 0 °C, 95%; (g) *m*-CPBA, DCM, −70 °C to rt., 95%; (h) NaN_3, DME/EtOH, H_2O, NH_4Cl, 0 °C, 95%; (i) MsCl, Et_3N, DCM, 0 °C, 68%; (j) PPh_3, Et_3N, THF/H_2O, rt.; (k) Ac_2O, pyridine, DCM, 0 °C, 65% after two steps; (l) $Cu(OTf)_2$, 3-pentanol, 0 °C, 48%; (m) H_3PO_4, EtOH, ref[223].

2.11 DECOMPLEXATION

Decomplexation of tricarbonyl iron complexes is usually achieved by oxidation, resulting in liberation of ligand without structural changes. The most common

reagent introduced in 1974 by Shvo and Hazum is trimethylamine-*N*-oxide (TMANO).[226] To a lesser extent copper(II) chloride[227], $FeCl_3$[228], cerium ammonium nitrate (CAN)[229], $Pb(OAc)_4$[230,231], H_2O_2/NaOH[232], MnO_2[231,104] and pyridinium chlorochromate[233] have also been used for this purpose. Demetallation of acyclic tricarbonyliron dienes was also accomplished by treatment with freshly prepared Raney nickel.[234]

The optimal method of demetallation depends on the structure and the reactivity of the substrate before and after decomplexation, as will be discussed later.

2.12 Conclusion

Iron tricarbonyl complexes imparted novel reactivity and selectivity to their attached organic ligands such as microbial diols thus providing unique opportunities to construct various organic molecules and natural products.

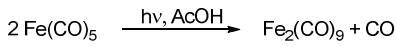
In future, preparation of enantiomarically pure iron tricarbonyl complexes will attract more attention.

Chapter 3
Iron complexation

CHAPTER 3: Iron complexation

As described in Chapter **1**, microbial oxidation of benzoic acid by *Ralstonia eutrophus* B9, is very effective to provide the corresponding (*1S,2R*)-diol **33** in high *e*.*e*.(>95%): this can undergo several novel synthetic transformations.[39] However, **33** had not been used in organometallic chemistry prior to the current work. We decided to explore the viability of forming iron carbonyl complexes of **33** and its derivatives.

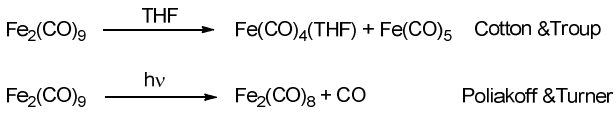
In order to do so, we used commercially available homoleptic binuclear $Fe_2(CO)_9$, which is more reactive and less toxic than $Fe(CO)_5$ (as it is a solid as opposed to a liquid). It was the first ever binuclear transition metal carbonyl synthesized.[235] It is made by photolysis of $Fe(CO)_5$ in acetic acid initiated by direct sunlight or a medium pressure mercury lamp.[236]



Scheme 60

Another preparation by Braye and Hubel was reported under the name diiron enneacarbonyl.[237] The reactivity of this compound is very important in organometallic chemistry.

There are two possible photolysis reactions of this binuclear iron carbonyl.[238,239]



Scheme 61

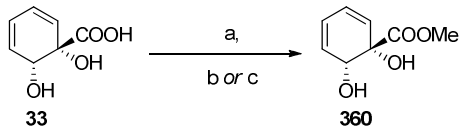
Cotton *et al*. reported that when complexation reactions were carried out in THF with diironnonacarbonyl, very reactive intermediates are formed.[240]

In the first instance, we employed the microbial diol acid **33** in attempted reactions with various carbonyliron species coordinated with various solvents, but these attempts were unsuccessful and the product mixtures became very complicated leading to intractable mixtures. We needed to keep in mind that **33** itself is unstable upon prolonged exposure to air and moisture at room temperature which leads to rearomatization products phenol and salicylic acid. (Chapter 1, Scheme **14**) In addition, the highly polar nature of the functional groups present (carboxylic acid, diol) rendered purification by silica chromatography impractical.

An alternative procedure was therefore sought. Thus esterification of the microbial diol acid to the corresponding methyl ester was investigated as a starting point of our endeavour. The reaction with (trimethylsilyl)diazomethane in benzene/MeOH under nitrogen can offer a swift method of methyl ester synthesis.[241,242] As hoped, the reaction mixture was converted to **360** in quantitative yield, after flash column chromatography.
From a safety point of view, use of TMS-diazomethane is preferable to diazomethane due to a reduced risk of explosion, but it is nevertheless just as toxic by inhalation.

A further drawback to use of (trimethylsilyl)diazomethane is cost. Thus, other procedures were attempted. Initial attempts to perform an esterification reaction with methyl iodide in DMF at room temperature resulted in formation of methyl ester **360** in poor 8% yield after purification on a silica gel column. Although the optimisation of this reaction was pursued, the yield did not increase significantly. In order to circumvent this problem, and increase the yield, we decided to search the literature for other applicable esterification methods. Sato *et al*. reported a practical CsF-promoted esterification of carboxylic acids at room temperature, although the use of long reaction times is required.[243] The (*1S,2R*)-diol **33**

reacted smoothly under mild conditions at room temperature, and the desired product **360** was furnished in a good yield of 72% after purification.



33 **360**

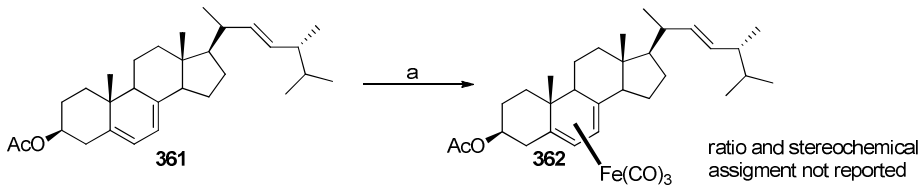
Scheme 62 Preparation of methyl ester **360.**

Reagents and conditions: (a) $TMSCHN_2$, rt., Benzene-MeOH (1:1), rt, N_2, 1 h, 100%; (b) MeI, DMF,NEt_3, N_2, rt., 23 h, 8%; (c) CsF (1.5 equiv), rt., DMF, MeI, N_2, 24 h, 72%.

The mechanism of this reaction remains unclear, but is possible that CsF acts as a base, and the hydrogen bonding is essential in the transformation of free acids into esters.

To the best of our knowledge, there are no prior reports of the use of an enantiomerically pure *nonannelated* cyclohexadiene ligand **33** possessing a quaternary centre for complexation with $Fe_2(CO)_9$. A relevant precedent dates from the late seventies, when Barton *et al.* reported diastereoselective complexation of ergosteryl acetate, giving the complex **362** in 69%. The iron tricarbonyl moiety was effectively protecting the diene in ring B of this steroid during hydrogenation of the C22-C23 double bond elsewhere in the structure (Scheme **63**). Multiple ergosteryl iron complexes (acetate and benzoate) were obtained, but stereochemical assignment was not undertaken.[244,245]

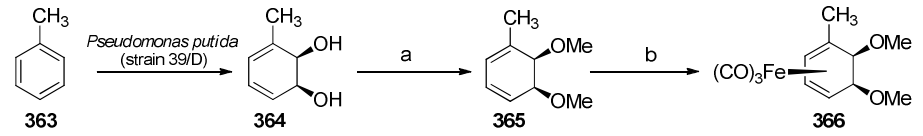
In a similar vein, the same group has demonstrated applications of this methodology in the formation of calciferol analogues. In this case stereochemical assignment of the iron complexes was by inference from the similar existing examples in the literature for the *endo*-directing hydroxy group.[246]



Scheme 63 Complexation of ergosteryl acetate

Reagents and conditions: (a) [$Fe(CO)_3$(bza)], ˣbza=benzylideneacetone, toluene, 90 ℃ 24 h, 69%.

Results reported by Stephenson *et al.* constitute a very important precedent, where several cyclohexadienyl diols were obtained by direct biooxidation of toluene and further elaborated to iron tricarbonyl complex **366**, possessing di-*endo* stereochemistry,[247] illustrating the effect of a hydroxyl group on facial selectivity. At the same time Stephenson has also reported a preparation of homochiral derivatives of toluene *via* microbial oxidation[248] and complexation to the iron tricarbonyl scaffold *endo* to the methyl ether (Scheme **64**).[247,249]



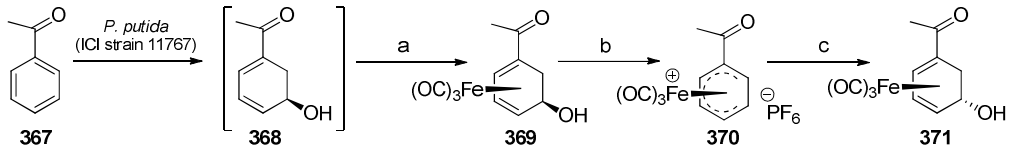
Scheme 64 Microbial oxidation of toluene and complexation of **365**.

Reagents and conditions: (a) MeI, KOH, 80%; (b) $Fe_2(CO)_9$, Et_2O, 34 ℃, 16 h, 53%.

Later Pearson *et al*. reported bio-oxidation of analogues of toluene to give (trifluoromethyl)cyclohexadienedienol products, and their manipulation towards novel enantiopure iron complexes; again, complete *endo* selectivity was observed.[112]

When employing acetophenone substrate, an anomalous monooxidation was observed to give unstable **368** manipulated *in situ* with diiron nonacarbonyl to give single diastereoisomer **369** after purification. In order to verify the stereochemistry of this product, additional steps were carried out to obtain well

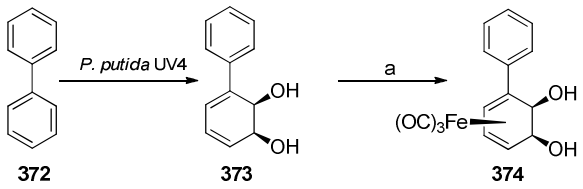
known complex **371**, by reaction with HPF_6 in acetic anhydride, giving cationic stable complex **370** in 86% yield after crystallization. Addition of an aqueous solution of sodium hydrogen carbonate, provided alcohol **371** as a diastereoisomer of **369** in 52% yield.[250]



Scheme 65 Preparation of alcohol **371**

Reagents and conditions: (a) $Fe_2(CO)_9$, THF, yield not reported; (b) HPF_6, Ac_2O, 86%; (c) $NaHCO_3$, H_2O, 52%.

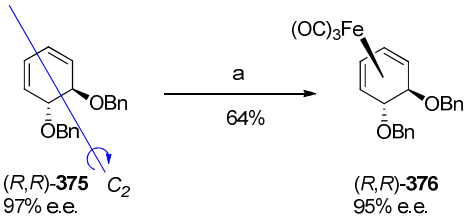
Most recently, in 2011, Stephenson *et al.* reported the synthesis of an enantiopure aryl-substituted organoiron complex **374** *via* microbial oxidation (*P. putida* UV4 mutant) of biphenyl, which was directly used for complexation in THF over 5 days. The yield was not reported. (Scheme **66**) The absolute stereochemistry of (1*R*,2*S*,3*S*)-stereoisomer was assigned by X-ray analysis where the irontricarbonyl moiety was on the same side as the *cis* diol.[251]



Scheme 66 Formation of organoiron complex **374**

Reagents and conditions: (a) $Fe_2(CO)_9$, 5 days, THF, yield not reported.

Suemune and co-workers reported[252] for the first time formation of chiral iron complex (*R*,*R*)-**376** without diastereoface selectivity because of the C_2 symmetry of the ligand.

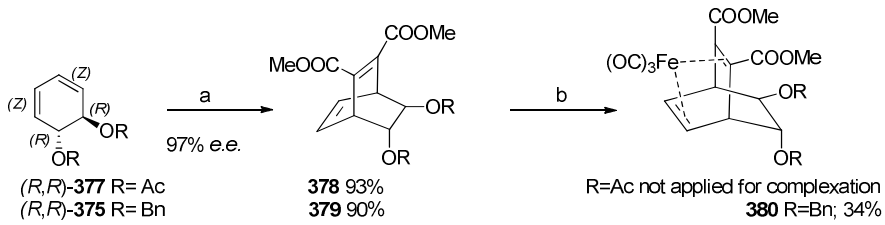


Scheme 67 Formation of chiral iron complex **(*R*,*R*)-376**

Reagents and conditions: (a) $Fe_2(CO)_9$, THF, reflux, 2 h, 64%, 95% *e.e.*

The reaction conditions were optimized and only the reaction over 2 h in THF with diiron nonacarbonyl (3.00 equiv) gave satisfactory results in the formation of (5,6-bis(benzyloxy)cyclohexa-1,3-diene)iron tricarbonyl complex in 64% yield. Surprisingly, prolonged reaction time decreased the *e.e.* of the complex **376**, probably due to the presence of acidic Lewis species from the $Fe_2(CO)_9$ source.

The same author, also reported further advances of this chemistry in the synthesis of novel optically active ligands 7,8-bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene **380** and its organoiron derivatives.[253]



Scheme 68

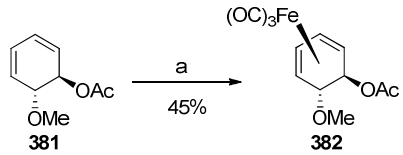
Reagents and conditions: (a) dimethyl acetylenedicarboxylate, benzene, reflux, 4 h, 93% for R=Ac, DCM, rt., 4 d, 90% for R=Bn; (b) $Fe_2(CO)_9$, THF, rt., Ar atmosphere, 4 h, 34%.

The corresponding tricarbonyliron complexes have also been synthesized in enantiomerically pure form. Reaction of (*R*,*R*)-**377** in basic conditions afforded the Diels-Alder product **378**, and was not submitted for metal complexation. Scheme **68**

In addition to the previously disscused results for chiral cyclohexadiene ligands in organoiron chemistry, more examples are known in the literature for non cyclohexadiene ring systems reported by Schmaltz *et al*.[254,255]
There are numerous examples existing in the literature of chiral iron tricarbonyl complexes obtained by direct nucleophilic addition to the cationic intermediates.

3.1 FACIAL STEREOSELECTIVITY

Berchtold and Ashworth reported the synthesis of iron complex **382** as a single isomer in 45% yield. The reaction was carried out in benzene at 55 ℃ with methoxyacetate **381** and (3-penten-2-one)iron tricarbonyl (*vide infra*).[256]



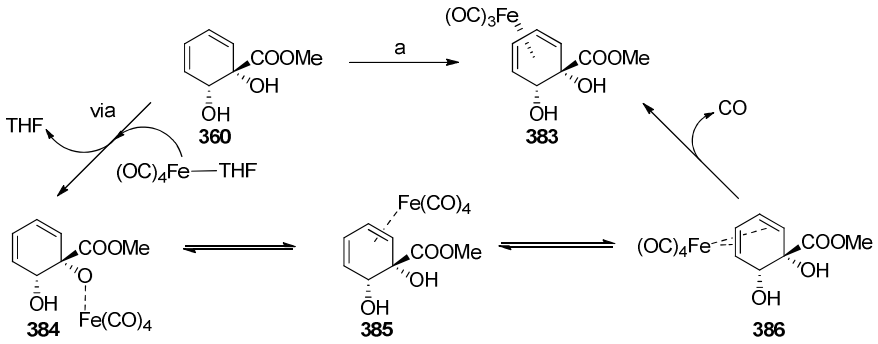
381 **382**

Scheme 69 Synthesis of single isomer **382.**
Reagents and conditions: (a) (3-penten-2-one)iron tricarbonyl, benzene, 55 ℃, 45%.

The importance of this result is that it is the only prior literature example showing the directing selectivity in a “competition ligand” (*i.e.* one in which both faces of the ring have Lewis basic groups). Other workers have reported that a methyl ester[257,95] could coordinate iron tetracarbonyl species to deliver *endo*-product after complexation on the same part of the molecule as the ester. In Berchtold’s case, the acetoxy group is a stronger directing group.

In our case, the thermally instable **33** scaffold possessing a quaternary centre, after esterification, was submitted to the complexation reaction of **360** with diiron nonacarbonyl in THF under nitrogen atmosphere *at room temperature*. After prolonged reaction it was transformed into the corresponding single isomer **383** in 55% yield after two steps. The iron carbonyl moiety approaches the same face

as the 1,2-diol to give product **383**, the structure of which was confirmed by X-ray crystallography (Appendix **1**). Similar attempts conducted in Et_2O provided desired product **383**, albeit in disappointing yield of 26%. This can be explained in terms of dissociation of diiron nonacarbonyl and the formation of THF–adducts with ironpentacarbonyl. We have searched for the best solvent but only THF seemed to give a satisfactory result.



Scheme 70 Complexation of **360**

Reagents and conditions: (a) $Fe_2(CO)_9$, THF, rt., 16 days, N_2, 55% over two steps.

We postulate that the mechanism involves the formation of an iron tetracarbonyl species **384** coordinated to the lone pair of oxygen either at the carbon C1 or C2, respectively, on the opposite side of the ring from the methyl ester. Unstable intermediates undergo decarbonylation to deliver final product **383**. This result indicates that the diol is a much stronger directing group than methyl ester.

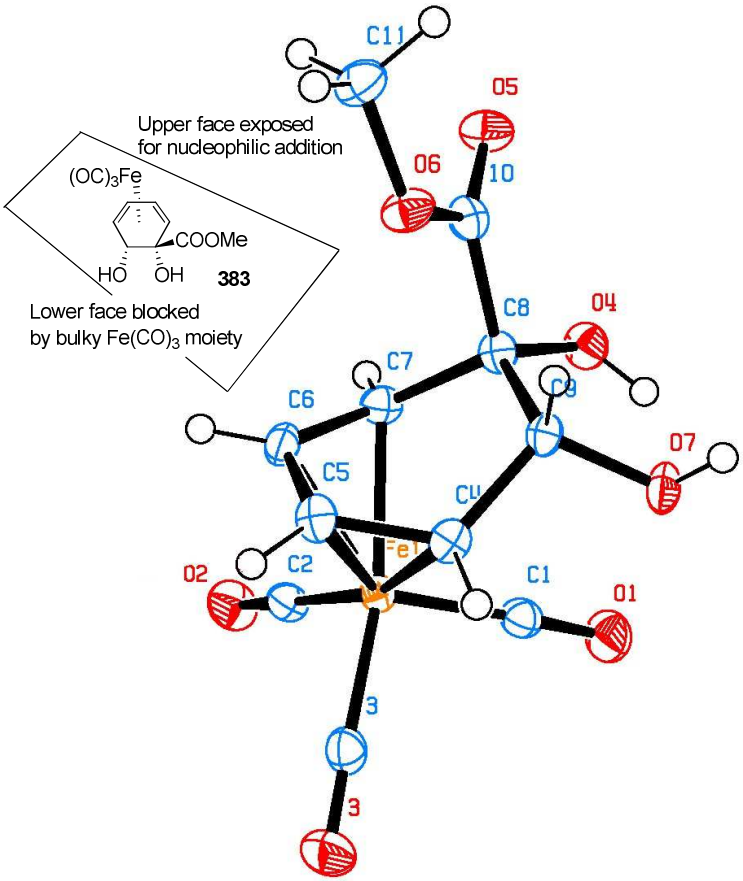
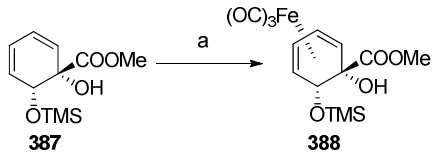


Figure 13 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **383.**

The crystal structure of **383** is shown in Figure **13**. The crystallographic data are summarized in Appendix **1.** The metal-ligand bonding arrangement conforms closely to that observed in other (1,3-cyclohexadiene)tricarbonyliron derivatives.[258] The iron atom is closer to the inner carbon atoms (C5-Fe=2.0628(18) Å, C6-Fe=2.0459(18) Å) than the outer ones (C7-Fe=2.0813(17) Å, C4-Fe=2.1037(17) Å), and the inner C5-C6 bond (1.406(3) Å) is shorter than the outer C8-C9 (1.564(2) Å), C7-C8 (1.526(2) Å) bonds.

The three CO groups are not equivalent, with one CO group lying over the “open” side of the *cis*-C4-C5-C6-C7 chain, while the other two lie over the outer C-C bonds. The mean Fe-C(carbonyl) distance of 1.79(8) Å is comparable to the many reported values (1.75-1.80 Å).[259] To within experimental error the four-atom diene set C4-C5-C6-C7 is accurately planar. In contrast, the C7-C8-C9-C4 set is slightly but significantly aplanar with a torsion angle of −2.94(19)º. The dihedral angle between the sets C8-C9 [44.9º] is larger than has been reported to date [36.3-40.6º], and [41.7-43.4º], respectively. The methoxycarbonyl set C11, O6, C10, O5 is planar and lies through the set. The hydroxyl substituent bonded to participates in a C8 hydrogen bond contact with the second hydroxyl-group O4-H4a-O7.

With the intention of increasing the yield of the reaction with TMS-diazomethane, the crude methyl esters were used directly for complexation, and surprisingly the formation of a second silylated co-product iron scaffold **388** was isolated in 22% yield. This was determined by the X-ray crystallographic structure of **388** (Appendix **1**).



387 **388**

Scheme 71 Formation of silylated co-product **388**

Reagents and conditions: (a) $Fe_2(CO)_9$, THF, rt., 14 days, N_2, 22%.

Precoordination of iron species plays an important role to deliver either *endo* or *exo* iron tricarbonyl complexes. In this case only the C1-hydroxy group was available for complexation of irontetracarbonyl to furnish unexpected product **388**.

Even after precomplexation of the tetracarbonyliron fragment the single available tertiary hydroxyl group still showed a stronger directing *endo* effect and overrode the effect of the ester.

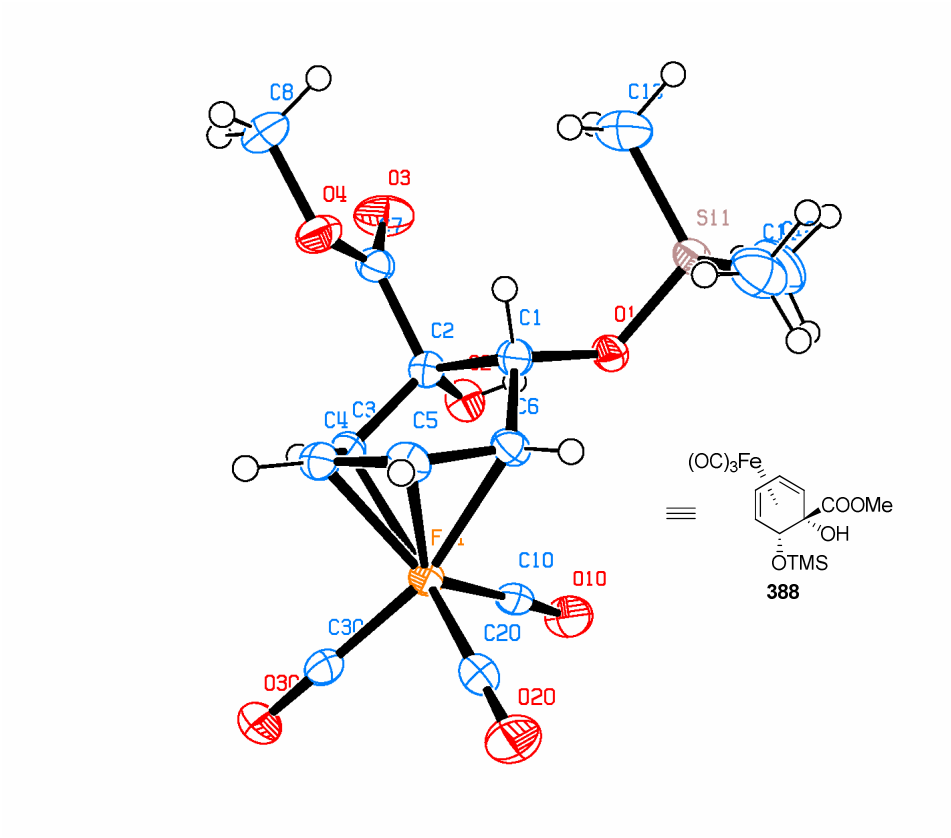
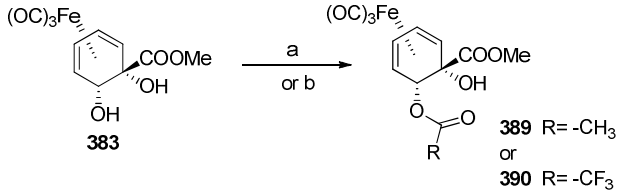


Figure 14 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **388.**

3.2 ELECTRONIC EFFECTS

Intrigued by these results of iron tricarbonyl complexes **383** and **388**, we decided to examine the scope of this chemistry further.

Herein, we report the synthesis of enantiopure scaffold, either bearing an acetoxy- (**393**) or the trifluoroacetoxy (**394**) group respectively. (Scheme **72**)



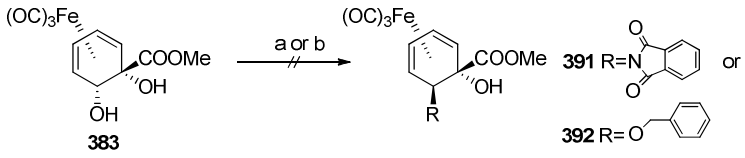
Scheme 72

Reagents and conditions: (a) Ac_2O, pyridine, −10 ℃, 18 h, N_2, 91% **389**; (b) TFAA, DCM, pyridine, −10 ℃, 23 h, N_2, 81%, **390**.

Treatment of complex **383** with acetic anhydride at −10 ℃ in pyridine as a reaction medium, afforded compound **389** after 18 hours of stirring in high yield 91%. A similar reaction was carried out, but with trifluoroacetic anhydride (TFAA) in DCM as a solvent, resulting in formation of **390** in 81% yield, which underwent spontaneous decomposition on silica gel column. Examination of the scope of these iron complexes towards nucleophilic addition reactions, through iterative η^4-η^{5+}-η^4 complex formation is described in Chapter **5**.

Further attempts to manipulate complex **383** towards direct introduction of new groups at C2 under Mitsunobu conditions, were unsuccessful. These reactions should invert the stereochemistry at the C2 carbon atom.

The Mitsunobu reaction was performed with DEAD (diethylazodicarboxylate) as a coupling agent, and triphenylphosphine in THF, followed by addition of iron complex **383** and phthalimide in THF. In an analogous fashion, replacing pthalimide with benzyl alcohol did not change the outcome of these attempts, and starting material was recovered in both attempts, instead of the desired product depicted in Scheme **73**.



Scheme 73 Attempted Mitsunobu reaction

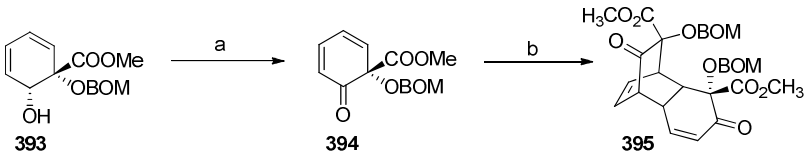
Reagents and conditions: (a) DEAD, phthalimide, 0 °C, 24 h, N_2, THF; (b) DEAD, benzyl alcohol, PPh_3, 0 ℃, 24 h, N_2, THF.

Those results persuaded us to find a new route to afford the desired product by formation of cationic iron frameworks described in detail in Chapter **5**.

3.3 OXIDATIONS

3.3.1 Synthesis of iron tircarbonyl cyclohexadienone 398

We next turned to an approach that the conversion of iron tricarbonyl methyl ester diol **383** to the corresponding ketone **396**, which would lead to a novel cyclohexadienone ligand not accessible by other means. Myers *et al*.[39] reported transformation of secondary alcohol of microbially derived methyl ester **393** by oxidation with Dess-Martin periodinane[260] in quantitive yield, after flash column chromatography. In the original paper, the authors were not able to oxidise the free diol **360** directly without decomposition, thus several protecting group stretegies were employed, where the –BOM ether (*via* multisep route) could deliver protected cyclohexadienone **394**. However, spontaneous Diels–Alder dimerization occurs at room temperature ($t_{1/2}$ = 4h), as shown in Scheme **74**.



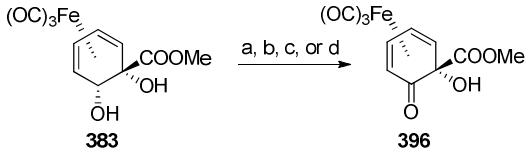
Scheme 74 Diels−Alder dimerization of **394**

Reagents and conditions: (a) DMP, pyr, DCM, rt, quantitive; (b) 23 ℃, ($t_{1/2}$) 4 h, initial concentration 0.6 M, $CDCl_3$.

Therefore it was desirable to find an alternative route to the synthesis of cyclohexadienone **396** which resembles that of **383**, but its dimerisation would be unable to take place due to it bearing an iron tricarbonyl moiety. Also, additional

protection of 1,2-diol was not required, and after demetallation a novel cyclohexadienone ligand would be readily accessible. Scheme **75**.

Nevertheless, our first choice of oxidant (Dess–Martin periodinane)[260] was not successful, and only starting material was recovered. Various reaction times, temperatures and quench procedures were carried out, for selective oxidation of **383**, but only a few were successful. Importantly, the oxidant must be *chemoselective*, because in most cases oxidation will liberate the ligand without structural changes (demetallation). In our case the oxidation should provided iron cyclohexanone **396** without cleavage of metal.



Scheme 75 Selective oxidation of iron complex **383**

Reagents and conditions: (a) Ph_3CBF_4, DCM, 26% (b) CrO_3, DCM, 2.5 h, rt, 9%; (c) PCC, DCM, 5 h, rt, 12%; (d) MnO_2, DCM, 24 h, r.t., 4 Å MS, 58%.

Triphenylcarbenium tetrafluoroborate is an oxidising agent which acts by hydride abstraction.[112] Attempted selective oxidation of the diol **383** was capricious, and furnished desired product **396** in yield 26%, after purification on silica gel column chromatography. Also, the trityl cation can act as dehydroxylating agent by coordinating to an alcohol, but for steric reasons (iron tricarbonyl moiety blocks approach of the bulky trityl cation) we did not noticed this process here.

The relatively low yield is tentatively attributed to demetallation, leading to the microbial methyl ester **360**, even with additional amounts of Cs_2CO_3. It was hoped that addition to the reaction mixture of DABCO (a base) would give the corresponding ketone **396**, but those attempts were also fruitless, and the starting material was recovered.

Therefore, other potential oxidations were examined, such as: TEMPO[261], and Swern[262]. No desired product was detected under any of these conditions. Attempts with Parikh-Doering oxidation[263] were low yielding (7%). Chromium(VI) compounds are highly toxic, and we decided not to pursue further with optimisations of those reactions.

Intriguingly, activated MnO_2 was demonstrated to be very effective[264] in the oxidation of diol **383**, leading to the corresponding iron ketone **396** in a repeatable yield of 58%, the structure of which was confirmed by X-ray crystallography (Fig. **15**, Appendix **1**). During the oxidation small quantities of water are produced and this could deactivate the surface of the MnO_2, therefore addition of active 4 Å MS was necessary.[265]

A long reaction time was required, and this was found to be beneficial. We have observed full conversion by monitoring the reaction by ^{1}H NMR, but the comparatively low isolated yield could be attributed to loss of product **396** on Celite® during purification and probably also on the surface of the excess of MnO_2 particles. The yield could perhaps be further improved by a reaction conducted with ionic liquids[266] and under sonication over prolonged time; this is currently under investigations in our lab.

Herein we report for the first time the oxidation of a cyclohexadienyl iron complex without decomplexation by manganese dioxide. In the literature only a few examples are known where MnO_2 was used for demetallation of the iron tricarbonyl fragment,[197] oxidation of *acyclic* dienes,[267] and of cyclobutadiene complexes.[264] In applications of organic chemistry it is used for the oxidations of allylic, benzylic and propargylic alcohols into the corresponding ketones or aldehydes (Ball-Goodwin-Morton reaction).[268] The iron complex **383** substrate could also be considered as an allyl alcohol.

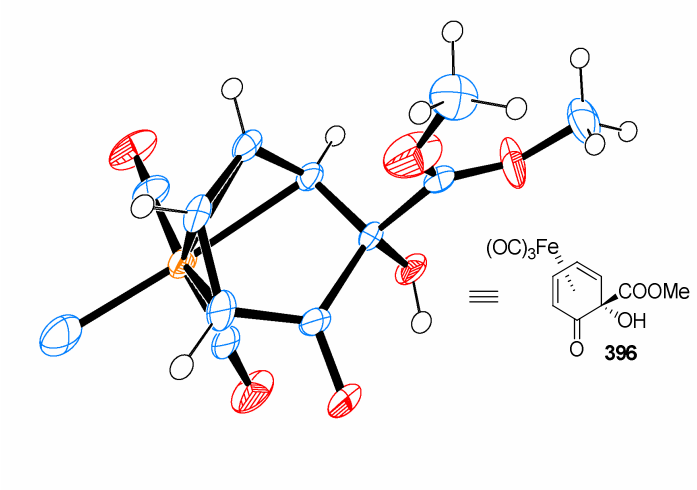
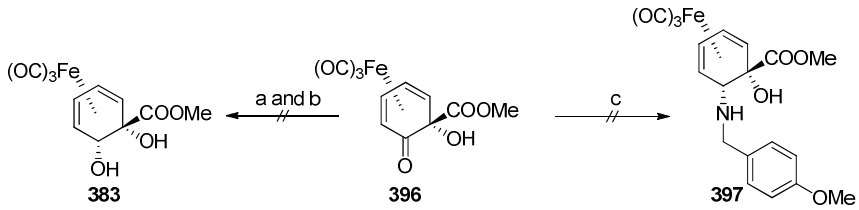


Figure 15 ORTEP diagram (50% probability factor for thermal ellipsoid) for **396.**

3.4 Reactivity of scaffold iron tricarbonyl-ketone 396

3.4.1 Reduction and PMB-derivatives

With **396** in hand, we turned our attention to obtaining *cis*-diol **383** by means of a direct reduction step. Initials attempts with L-Selectride,[269] followed by TLC monitoring, showed incomplete consumption of starting material and hence proved futile. Several new spots appeared but we were unable to unambiguously identify the products formed. Attempts to convert **396** to **383** using sodium borohydride also met with failure resulting in complete loss of material. Additionally, decomposition occurred when **396** was treated with acetic acid, followed by addition of PMB-amine and treated with sodium triacetoxyborohydride overnight at room temperature and then heating to reflux; no complex **397** was obtained. Scheme **76**

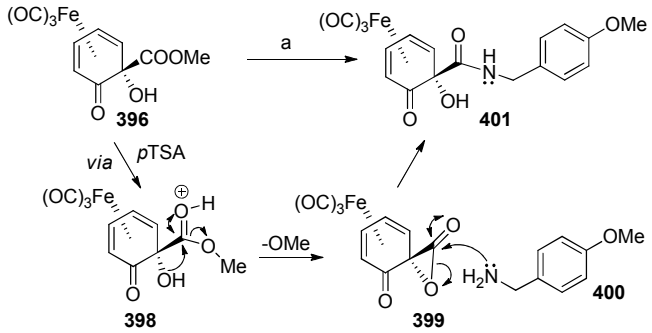


Scheme 76 Attempted reduction of iron ketone **396**

Reagents and conditions: (a) L-Selectride (1M in THF), −78 ℃, THF, 9 h, N_2; (b) $NaBH_4$, MeOH, N_2, rt, 5 h; (c) AcOH (1.0 equiv), THF, PMB-amine (2.00 equiv), $(AcO)_3BHNa$ (2.00 equiv), N_2, rt→80 ℃, 24 h.

The aim of this experiment was to form an imine that subsequently could be reduced to the amine and demetallation would provide an amino alcohol.

It was interesting to note that the reaction between PMB-amine and iron ketone **396** in diethyl ether, at *room temperature*, with a catalytic amount of *p*TSA delivered a new product **401**. The reaction was stirred overnight and indicated only starting material in the reaction mixture by ^{1}H NMR. Thus, it was left to stir for an additional 9 days with activated 4 Å MS, following it by TLC. Subsequent purification on a silica gel column surprisingly led to isolation of novel iron complex **401**, albeit in low yield (8%) Scheme **77**.



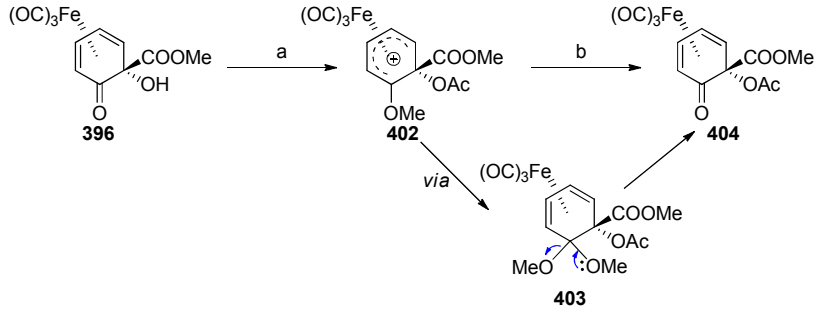
Scheme 77 Formation of PMB-derivative product **401.**

Reagents and conditions: (a) *p*TSA, Et_2O, PMB-amine **400** (1.05 equiv), rt, 9 days, 4 Å MS, (8%).

It is believed, that an α-lactone **399** is produced by methoxy group elimination after hydroxy group (C1-OH) attacking protonated carbonyl group of methyl ester **398** to form an intermediate with three-membered ring of a cyclic ester **399**, which upon treatment with PMB-amine **400** undergoes ring opening to deliver final product **401**.[270,271,272]

3.4.2 Preparation of Meerwein's salts

Encouraged by the preliminary results obtained using *p*TSA we wished to extend the scope of this methodology through to an alkylation with trimethyloxonium tetrafluoroborate,[273,274] as this would allow the preparation of more stable cationic derivatives from iron ketone **396**.

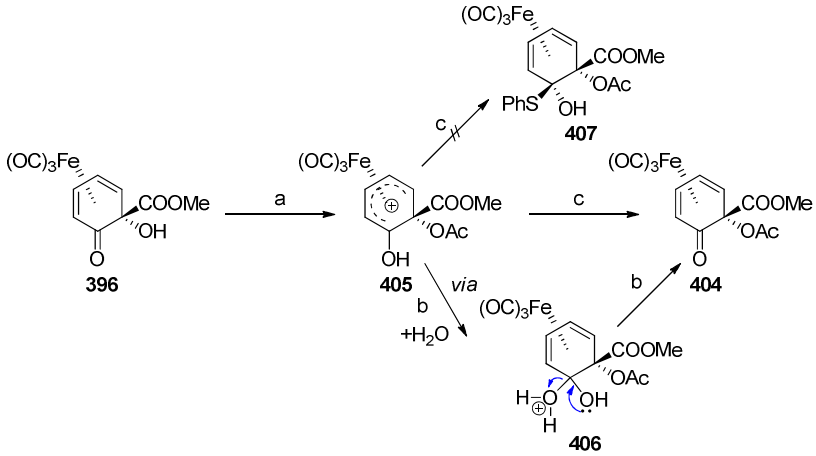


Scheme 78 Formation of methoxy substituted intermediate with Meerwein's reagent. Reagents and conditions: (a) Me_3OBF_4, Ac_2O, −10 °C, N_2, 1 h, (b) NaOMe, MeOH, 24 h, −10 °C →rt, (83%) over two steps.

It was possible that the conversion of the iron ketone **396**, by direct treatment with trimethyloxonium tetrafluoroborate in Ac_2O at −10 °C, could be achieved, leading to **402**, which underwent nucleophilic attack upon treatment with sodium methoxide in MeOH, and subsequent hydrolysis to provide **404** in 83% yield over two steps.

The putative intermediate **402** could not be isolated, but this pathway is feasible, and this reaction sequence might be useful in formation of acetylated cyclohexadienyl ligands at C1 carbon atom.

Encouraged by the formation of possible cationic species of **402**, we decided to further examine further the scope of this reaction.



Scheme 79

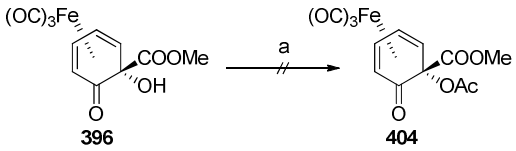
Reagents and conditions: (a) Ac_2O, −12 ℃, HBF_4-OEt_2, N_2, 1 h; (b) *aqueous* work up, 96% (c) NaSPh, 0 ℃, THF, 2 h, 64% (*aqueous* work up).

A solution of iron ketone **396** in acetic anhydride was treated with HBF_4-OEt_2 at −12 ℃, followed by aqueous work up, and provided a cetylated product **404** in high yield (96%). The reaction was attempted in a similar fashion, leading to cationic intermediate **405**, which upon treatment with sodium thiophenolate gave the same acetylated product **404** in 64% yield after column chromatography. Aqueous work up of the reaction mixture or some traces of water caused the hydrolysis of the cationic intermediate **405**, scheme **79**.

The unexpected product **404** is not accessible by straight forward acetylation of neutral complex **396,** thus cationic intermediate step is essential to furnish it.

To prove the use of this approach additional studies were conducted, and the attempted synthesis of **404** was carried out in a manner similar to that used

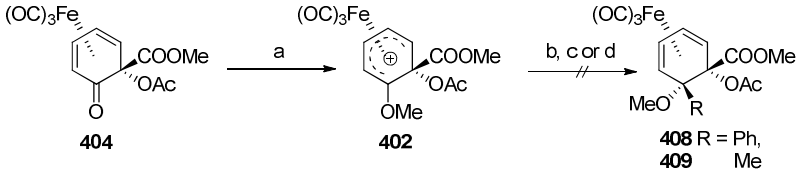
previously, but trimethyloxonium tetrafluoroborate or acid were not introduced at any stage. With this change of approach, the reaction did not lead to the required product, and starting material was recovered (*vide infra*). In this case, the only method of the acetylation of C1-OH is achieved through formation of η^5-cyclohexadienyl intermediates (**402** or **405**) followed by hydrolysis, (scheme **80**).



Scheme 80 Attempted acetylation of complex **396** at C1**.**
Reagents and conditions: (a) Ac_2O, −10 ℃, N_2, 1h.

Faced with this setback, we decided to perform the *O*-alkylation reactions on the more stable acetylated scaffold **404**. However, the attempted introduction of a phenyl or methyl group was unsuccessful, giving recovered starting material in all cases, as depicted in scheme **81**.

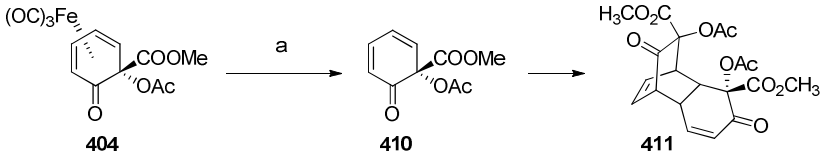
It could therefore be concluded that the presence of the ketone group plays a significant role on the electronic effect of the whole molecule **404**, but a detailed understanding of these observations is still lacking.



Scheme 81 *Attempted O-alkylation of methoxy-intermediate* **402**.
Reagents and conditions: (a) Me_3OBF_4, CH_3CN, −10 °C, 1 h; (b) PhLi, DCM, 2h, −78 °C; (c) PhLi, THF, 2 h, −78 °C; (d) CH_3Li, CuI, THF, 0 ℃, 1 h.

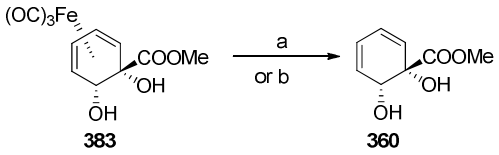
3.4.3 Attempted demetallation reactions of iron tricarbonyl cyclohexadienone 396 and 404

Various attempts to deprotect irontricarbonyl ketones **396** and **404** failed, such as use of $CuCl_2$ in EtOH or TMANO in acetone; only for **404** conditions employing CAN (10.0 equiv.) in acetone afforded dimerisation product **411**. This was observed by analysis of mass spectrometry confirming formation of the required product (m/z HRMS (+ve ESI-TOF) m/z calcd for $(C_{16}H_{17}O_8)^+$, 337.0923; found 337.0897, for $(C_{16}H_{16}O_8Na)^+$, 359.0748; found 359.0722), but unfortunately it was unstable during purification by flash column on silica gel chromatography. In our lab, we were unable to cleanly deliver demetallated cyclohexanone **411**.



Scheme 82 Attempted demetallation of irontricarbonyl acetylated ketone complex **404.**
Reagents and conditions: (a) CAN (10.00 equiv), acetone, 0 ℃ →rt, 23 h.

In contrast to the ketone complex, upon addition of the diol methyl ester complex **383** to a solution of TMANO in benzene, then stirring for 24 h at room temperature, the desired product **360** was afforded in 54% yield after purification.



Scheme 83 Demetallation with TMANO or CAN iron tricarbonyl scaffold **383.**
Reagents and conditions: (a) TMANO (6.00 equiv), benzene, rt, 24 h, 54%. (b) $(NH_4)_2Ce(NO_3)_6$, 3.00 equiv., acetone, 0 ℃, 15 min; 90%.

Also, treatment of **383** with CAN in acetone for 15 min gave **360** as a white powder in 90% yield. Analytical data agreed with literature values.[39]

3.5 Conclusions

To summarize our results, we have shown the utility of the complexation reaction towards enantiomerically pure microbially-derived cyclohexadiene ligands possessing a quaternary centre and their modification post-complexation to give derivatives.
Additional investigations of silylated cyclohexadiene ligands to prevent the formation of the *endo* metallated product proved unsuccessful.

Regrettably, several attempts to access a dienone with various oxidising agents proved unsuccessful, however the successful oxidation with activated MnO_2 led to stable irontricarbonyl ketone **396** in good yield. Nevertheless **396** proved to be unreactive in most subsequent transformations.
Subsequent X-ray crystallographic studies confirmed the structures and stereochemical assignment of **383** and **396**.
The demetallation could be achieved on both complexes, although only the Diels–Alder dimer was detected after decomplexation of irontricarbonyl ketone.

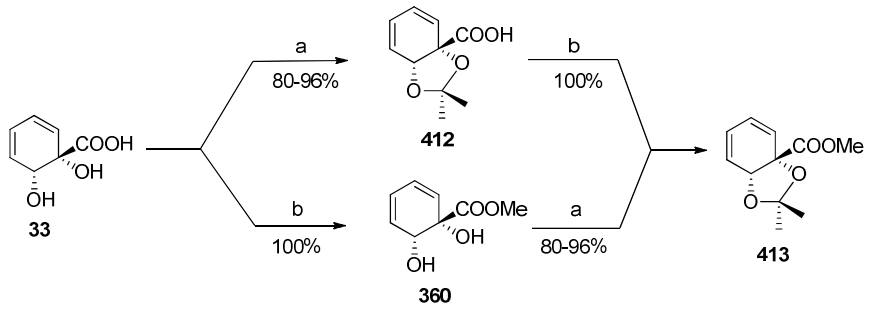
Some of the results presented in this Chapter were published as a paper in Organometallics.[53]

Chapter 4
Rearrangement

CHAPTER 4: REARRANGEMENT

Having successfully synthesised the diol-containing complex **383** where the iron tricarbonyl moiety was *endo*, the focus of our efforts shifted to the synthesis of a complex where diol was *exo*, by protecting the diol as an acetonide. We assumed that the additional steric hindrance of the lower face would disfavour the formation of a precoordinated iron intermediate and iron would undergo top face coordination.

As depicted in Scheme **84**, protected acetonide **413** was prepared in just two steps, either by direct conversion into the corresponding methyl ester **360**, further exposed to the catalytic amount of *p*-toluenesulfonic acid and 2,2-dimethoxypropane in acetone, or by reversing the order of addition of the substrates, to furnish desired product **413** in high yield.

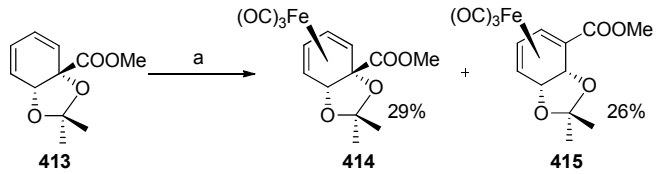


Scheme 84 Synthesis of acetonide protected **413.**

Reagents and conditions: (a) PTSA (cat.), DMP, acetone, rt, 2 h; (b) $TMSCHN_2$, rt, Benzene-MeOH(1:1), rt, 1 h, 100%.

Reaction with a slight excess of diironnonacarbonyl in THF at ambient temperature for 7 days resulted in the generation of a complex mixture of starting material and two products, which were purified by a silica gel column chromatography. It was fascinating to note that indeed the *exo* product **414** (29%) was formed, along with the novel, unexpected rearrangement product **415**,

in 26% yield, (Scheme **85**). The structures were confirmed by X-ray crystallography (Appendix **1**).



Scheme 85 Formation of unexpected rearrangement product **415**.
Reagents and conditions: (a) $Fe_2(CO)_9$ (1.09 equiv.), THF, rt, 7 d.

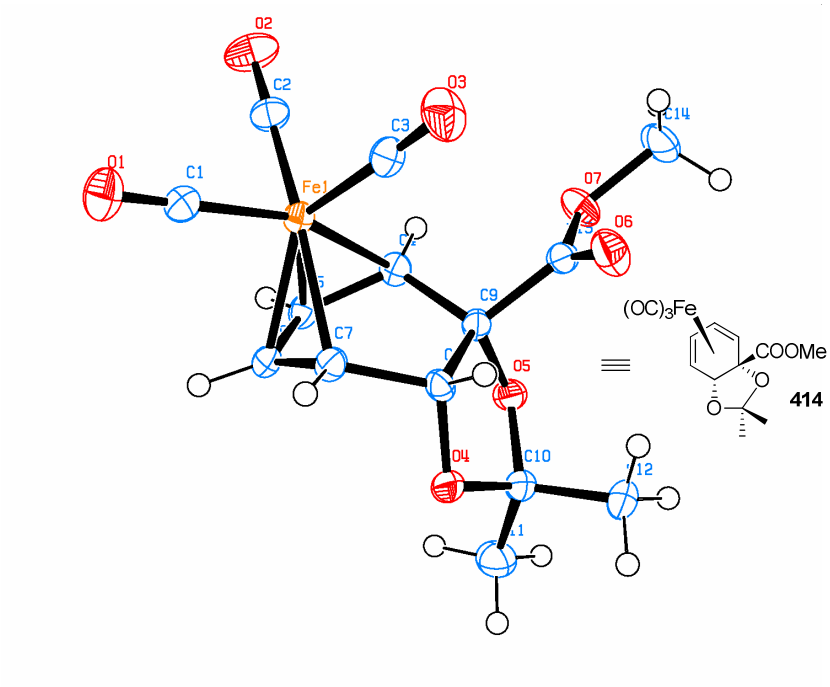


Figure 16 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **414.**

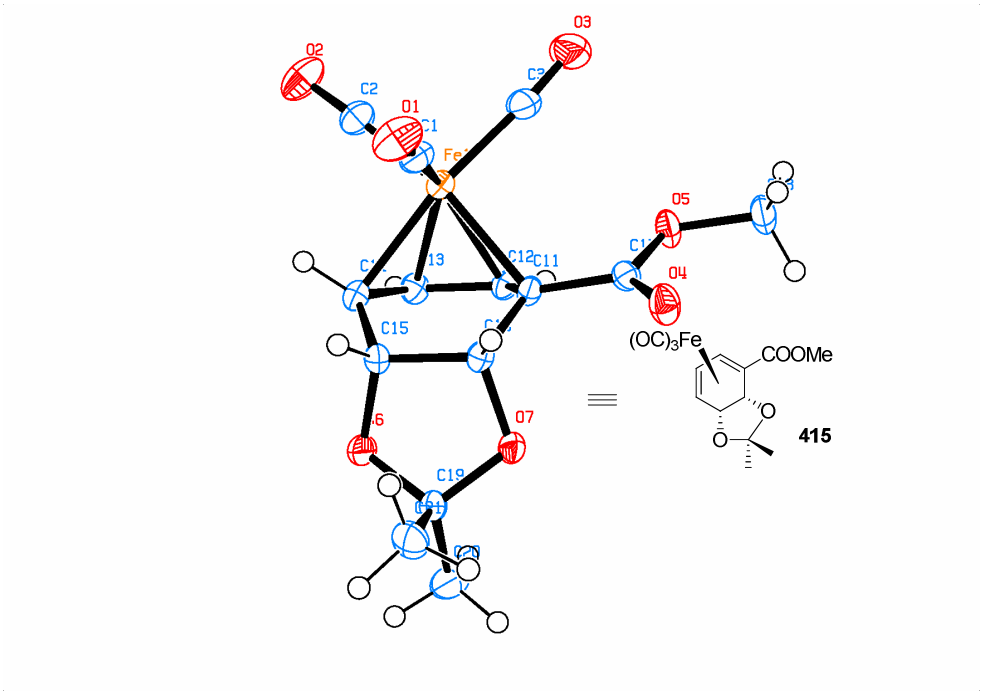
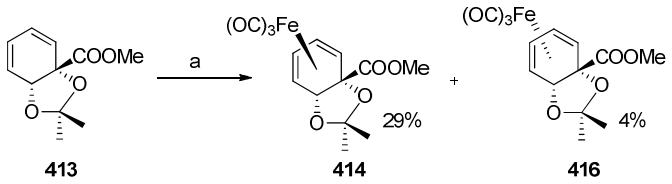


Figure 17 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **415.**

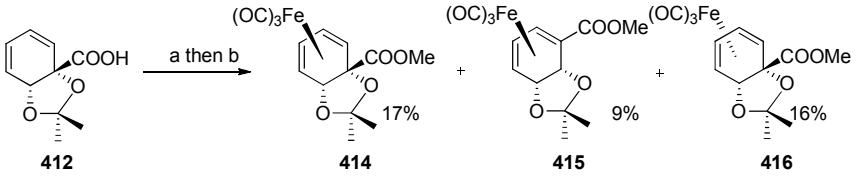
When the reaction was repeated with 1.00 equivalents of diironnonacarbonyl it did not give rise to the rearrangement product, but *endo* iron complex **416** was isolated in a very low yield of 4% in addition to *exo* complex **414** (29%).
The reaction was capricious, sometimes leading to conjugated product **415**.



Scheme 86 Iron complexation of acetonide protected **413**
Reagents and conditions: (a) $Fe_2(CO)_9$ (1.00 equiv.), THF, rt, 7 d.

Reversing the order of events by effecting complexation of the acetonide protected free acid **412** (with *subsequent* esterification) did not improve the yield of the reaction. Interestingly, however, it resulted in the formation of all three

products including the rearrangement product **415** every time. Also other conditions were investigated, such as reversing the order of addition of starting materials, but those reactions were poor yielding and not reproducible.



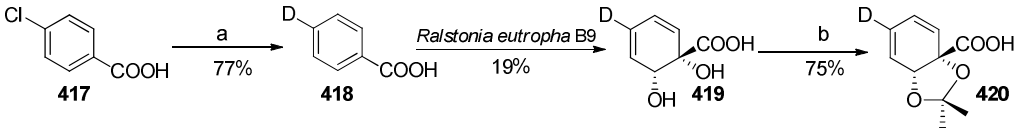
Scheme 87 Iron complexation of acetonide protected acid **412** followed by esterification
Reagents and conditions: (a) $Fe_2(CO)_9$ (1.00 equiv.), THF, rt, 8 d; (b) $TMSCHN_2$, rt, Benzene/MeOH (1:1), rt, 1 h.

4.1 Mechanism

We postulated that rearrangement of **414**, was occurring by way of "clockwise" migration of the acetonide protecting group rather than "anticlockwise" migration of the carboxymethyl group.

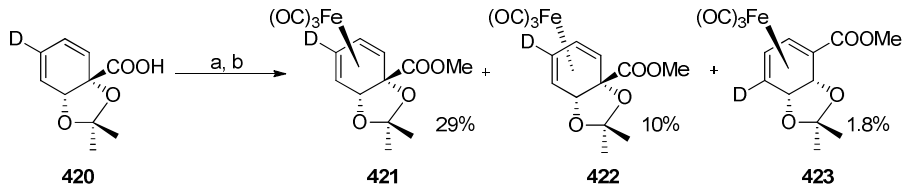
To probe the mechanism of formation of the novel rearrangement product, studies with labelled compounds were employed. Commencing from *p*-chlorobenzoic acid, dehalogenation with deuterium gas proceeded smoothly to give **418** in a reasonable yield of 77%.[275]

Following Myers' procedure for the microbial oxidation[39], but employing *p*-deuterobenzoic acid **418** as substrate gave **419** in a yield of 19%.



Scheme 88 Synthesis of labelled acetonide protected microbial diol acid **420**
Reagents and conditions: (a) 10% Pd/C, D_2O, Et_3N, rt, 48 h, 77%; (b) *p*TSA (cat.), DMP, acetone, rt, 2 h, 75%.

With a supply of **419** in hand, we proceeded as shown in schemes **88** and **89**. Conversion of **419** to acetonide **420** was accomplished with DMP and *p*TSA in 75% yield, followed by direct esterification of the crude with TMS-diazomethane. Then the product was treated with diiron nonacarbonyl in THF for 8 days, giving a mixture of three different components (**421-423**) after further purification on a silica gel column.



Scheme 89 Synthesis of labelled rearrangement product **423**

Reagents and conditions: (a) $Fe_2(CO)_9$ (2.17 equiv.), THF, rt, 9 d; (b) $TMSCHN_2$, rt, Benzene/MeOH(1:1), rt, 50 min.

Variations in chemical shift are observed upon comparison of the rearranged (**423**) and non-rearranged complex (**421**). Shifts in the conjugated olefinic system C-H5 signal from 6.13 ppm to 5.71 ppm and C-H6 from 5.81 ppm to 6.36 ppm in the ^{1}H NMR spectrum confirmed successful synthesis of the desired *rearranged* ^{2}H-labelled methyl ester **423**. Moreover, an analysis of the splitting pattern for C-H5 and C-H3 in the labelled product **423** showed separate doublets instead of a triplet, and doublet of doublets, respectively. Also, most tellingly, in the deuterated cyclohexadiene system C-H4 is absent, whereas in the non-deuterated system it is observed as a doublet of doublets at 3.11 ppm (*vide infra*). From an above analysis the formation of a second product **424**, after the methyl ester migration was not noticed.

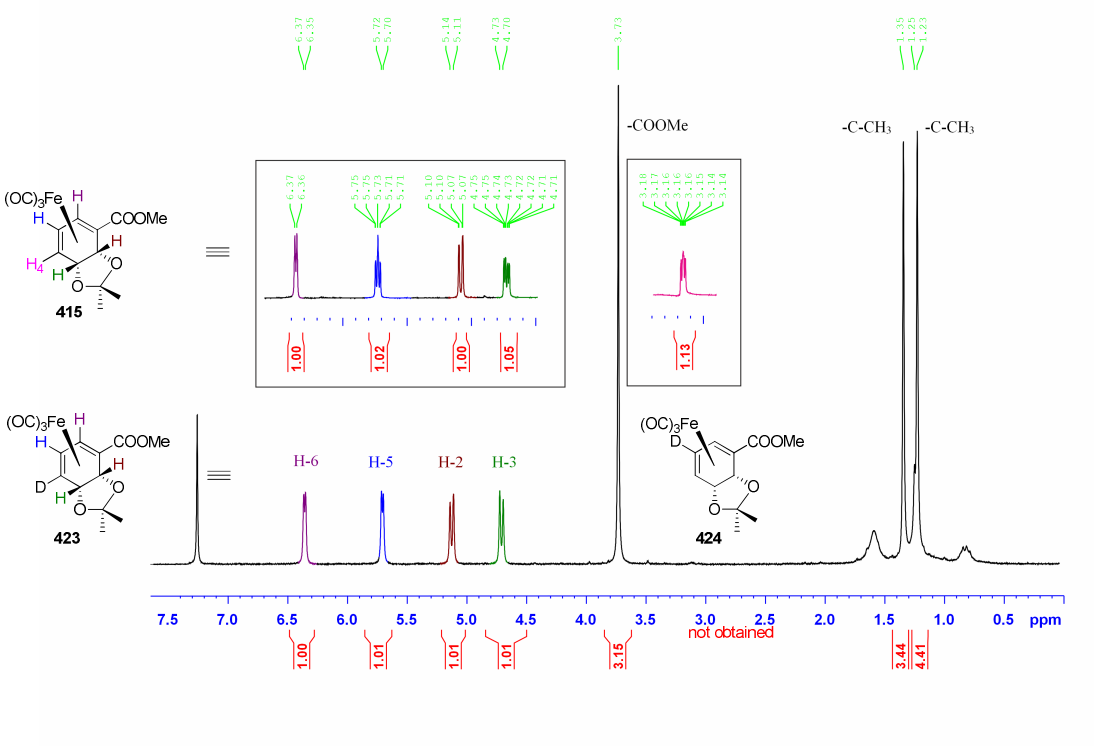


Figure 18 ^{1}H NMR spectrum for deuterated product **423.**

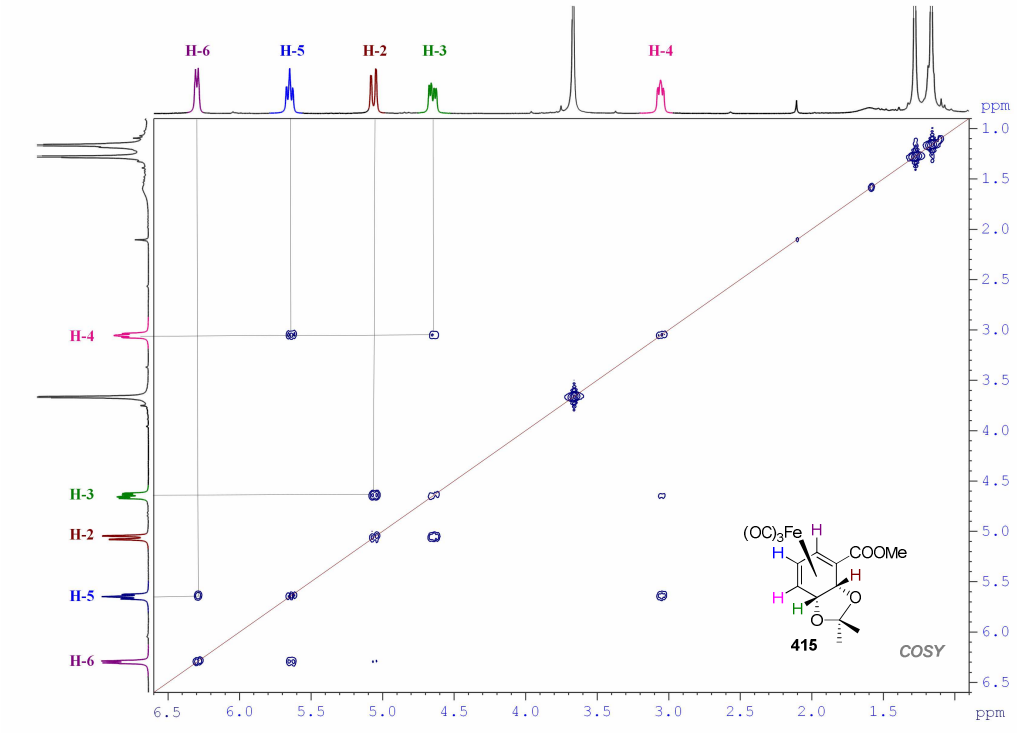
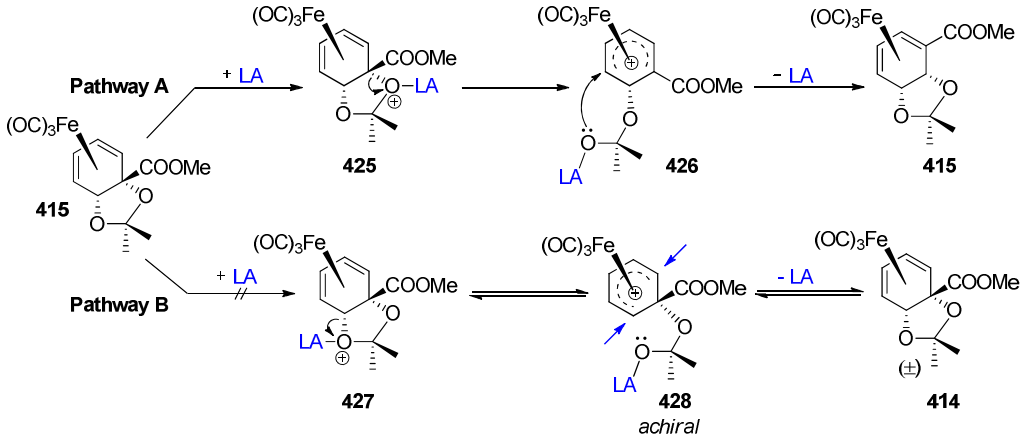


Figure 19 *COSY* spectrum for non-deuterated product **415.**

These studies strongly suggested that the rearrangement was taking place by an "anticlockwise acetonide migration" mechanism and not a "clockwise ester migration" mechanism.

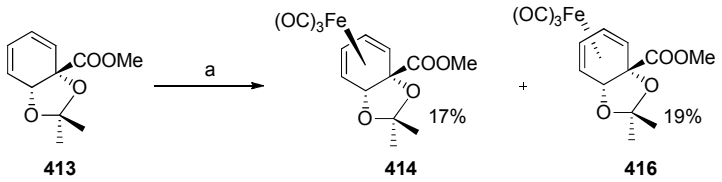
The mechanism we propose invokes cationic η^5 intermediates in order to furnish conjugated product **415**. We believe that an unknown Lewis acid is present (perhaps a coordinatively unsaturated iron species) and is a key factor to form more stable **426** due to steric strain relief upon rehybridisation of C1 from sp^3 to sp^2 where the methyl ester group is coplanar with the dienyl system. The Pathway **A** was taking place rather than Pathway **B**, because the structure **415** was found to be *not* racemic (*vide infra*), whose identity was established by X-ray crystallographic analysis. (Appendix **1**). If Pathway **B** was operative, it would result in racemisation of the starting material **414** (and hence give a racemic product **414**) because cation **428** is *achiral*.



Scheme 90 Proposed mechanism for iron mediated isomerisation by Lewis acid.

Hence, we sought an alternative method to obtain the conjugated product **415** in higher yield. Since the proposed mechanism is catalysed by a Lewis acid, we believed that addition of Brønsted acid would improve the yield significantly, thus an attempt at a one-pot complexation/rearrangement with addition of *p*TSA into

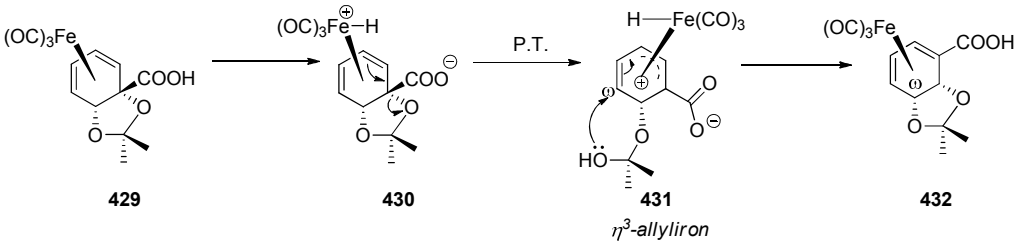
the reaction mixture. The reaction was conducted in THF and diironnonacarbonyl for 12 d, and then followed by addition of 40 mol% of *p*TSA for 7 days, as shown in scheme **91**. This attempt, met with failure and rearrangement product **415** was not obtained under these conditions.



Scheme 91 Attempted synthesis of conjugated complex **415**

Reagents and conditions: (a) $Fe_2(CO)_9$ (1.50 equiv.), THF, rt, 12 d, then *p*TSA (40 mol%), additional 7 d.

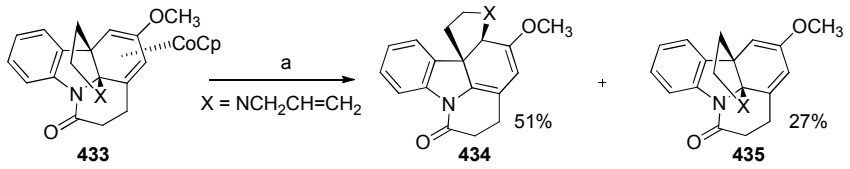
Finally, the last example, where the compound **432** was furnished, after iron complexation of **412**, could conceivably be an autocatalytic process, proceeding by the formation of kinetic η^3-allyliron product **431**. A plausible alternative mechanism accompanying isomerisation, could take place through the protonation of the $Fe(CO)_3$ tripod, and formation of kinetically stable product **431**, which would allow for the unusual acetonide group migration by nucleophilic addition to the ω-position to deliver the final stable complex **432**.[95,276]



Scheme 92 Proposed mechanism for a autocatalytic acetonide migration inducted by acid.

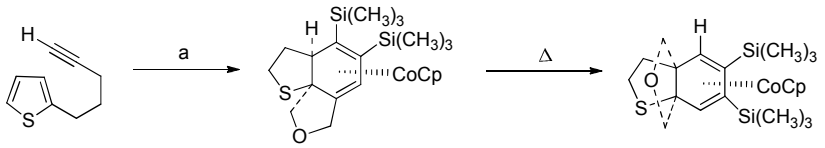
To the best of our knowledge we are not aware of any such example where acetonide migration is mediated by an iron tricarbonyl tripod in the literature.

There are some known examples where a cobalt Cp complexes can induce such a rearrangement[277] (Scheme **93**). It was found, that standard oxidative demetallation of **433** gave desired product **435** (27%) but also rearrangement skeleton **434** in 51%.



Scheme 93 Demetallation of cobalt Cp complex **433.**

Reagents and conditions: (a) $CuCl_2 \cdot H_2O$, 5 equiv., Et_3N (2.0 equiv.), 1,2-dimethoxyethane−H_2O, 0 ℃, 51%.



Scheme 94 Cobalt mediated [2+2+2]cycloaddition of **436.**

Reagents and conditions: (a) BTMSA (5 equiv.), toluene, 23 ℃, CpCo ($C_2H_4)_2$, providing **437** (8%) and **438** (25%).

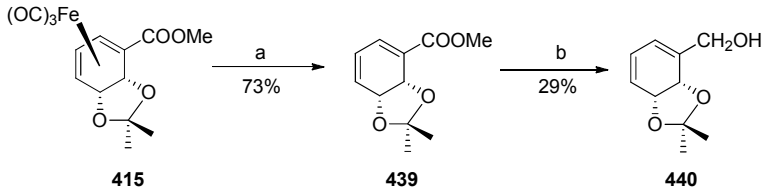
Volhard *et al*[278] have reported cobalt mediated [2+2+2]cycloaddition of **436** with solvent bis(trimethylsilyl)acetylene providing a series of rearrangement products, (Scheme **94**).

4.2 Determination of e.e.

The determination of *e.e.* of the rearrangement product **415** was required in view of the potential for erosion of *e.e.* via "Pathway **B**" (*vide supra*). Many methods of determining of *e.e.* values are known such as GC or HPLC with a chiral column chromatography and NMR techniques.

Currently a widely used method is Mosher's procedure[279,280,281] for alcohols and amines that employes MPTA. The applicability of both ^{1}H and ^{19}F NMR to the products is an advantage as it increases the likelihood of finding a diagnostic resonance to integrate.

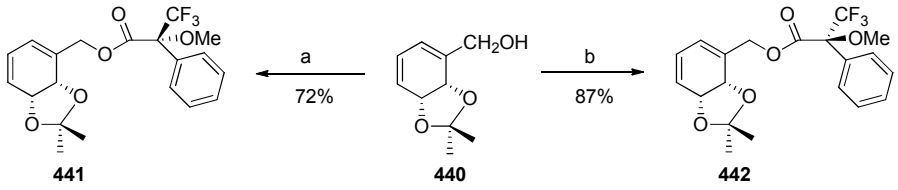
With **415** in our hand as obtained previously, demetallatation was conducted using TMANO in benzene at room temperature to deliver uncomplexed **439** in 73% yield.



Scheme 95 Demetallation and reduction of **424** complex.

Reagents and conditions: (a) TMANO, benzene, rt, 5 h (73%); (b) $LiAlH_4$, Et_2O, 15 min at −84 °C →rt 30 min, then Rochelle's salt, 1 h, rt, (29%).

Upon subjection of **439** to $LiAlH_4$ reduction, primary alcohol **440** was isolated (29%), followed by direct treatment of the resultant alcohol **440** with (+)-MTPA, and (−)-MTPA (CH_2Cl_2/DIC/DMAP).



Scheme 96 Preparation of Mosher's esters.

Reagents and conditions: (a) (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate (Aldrich #155268, 99% *e.e.*), (2.00 equiv.), DIC (2.00 equiv.), DMAP (0.15 equiv.), DCM, rt, 17 h, (72%); (b) (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate (Aldrich #155616, 95% *e.e.*), (2.00 equiv.), DIC (2.00 equiv.), DMAP (0.09 equiv.). DCM, rt, 17 h, (87%).

From the NMR investigation of the both products the ^{19}F-NMR of the derived MTPA esters **441** and **442** showed a single resonance at −7.51 ppm. However, the ^{1}H-NMR spectrum was much more useful, as the diastereotopic methylene

protons provided a diagnostic resonance which did not overlap any other resonances.

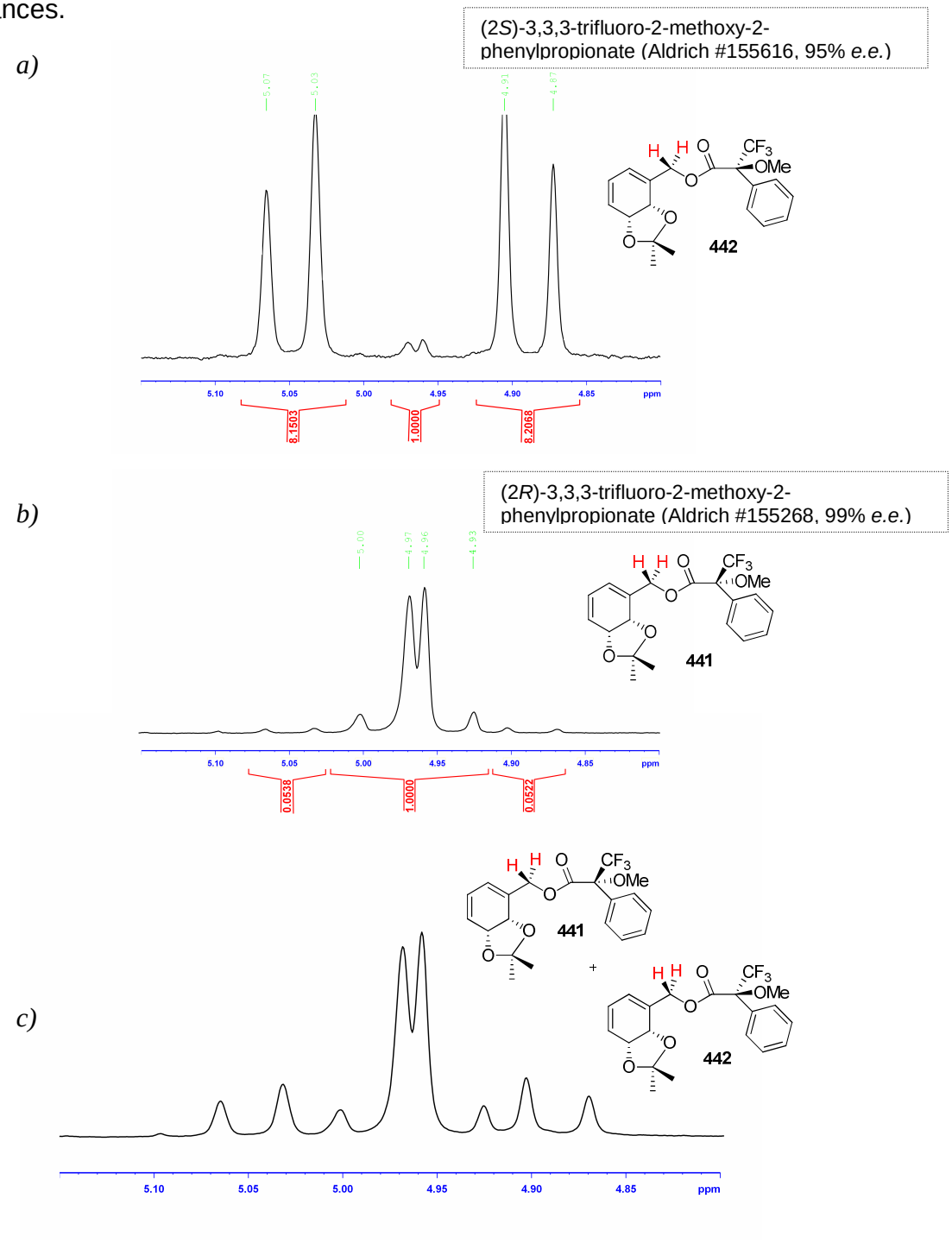
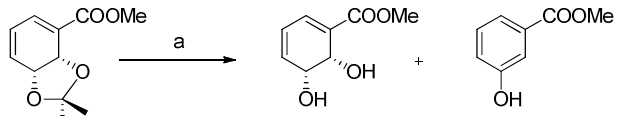


Figure 20 ^{1}H–NMR studies of Mosher's esters **441** and **442**

From the above spectra, it can be discerned that the *e.e.* of **415** is >95% and therefore racemisation by "Pathway **B**" in Scheme **90** is minor.

4.2.1 Deprotection of acetonide

We wished to explore the feasibility of removing the acetonide and unmasking the free diol in **439**. Initial experiments were carried out using catalytic AcOH or Dowex® 50WX8 but were unproductive, resulting in the formation of an aromatic product **444**. However, partial success was obtained in an attempt by treatment of the solution containing **439** with I_2 in CD_3OD in a Young's NMR tube, and heated up to 50 ℃ resulting in direct product formation (Scheme **97**).[282,283] ^{1}H-NMR spectra were acquired at five minute intervals revealing formation of the product **443**. Unfortunately before all acetonide removal had occurred, rearomatisation began to occur and ultimately all material aromatised to give **444**.



439 **443** **444**

Scheme 97 Formation of (2S,3R)-methyl 2,3-dihydroxycyclohexa-4,6-dienecarboxylate **443** observed by ^{1}H-NMR.

Reagents and conditions: (a) I_2 in CD_3OD in a Young's NMR tube, 50 ℃.

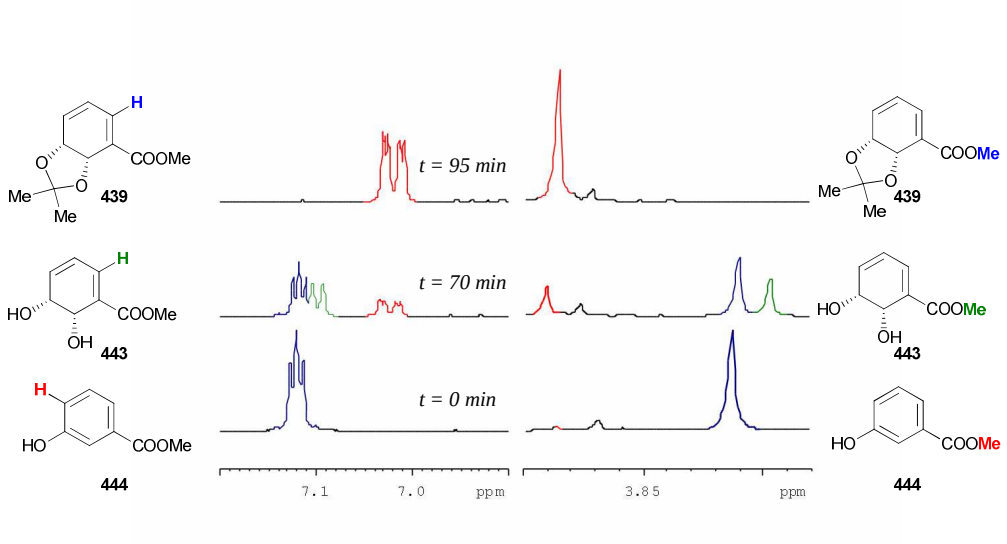


Figure 21 NMR spectra of iodine-mediated deprotection of **439** at specific time points. Peak assignments shown.

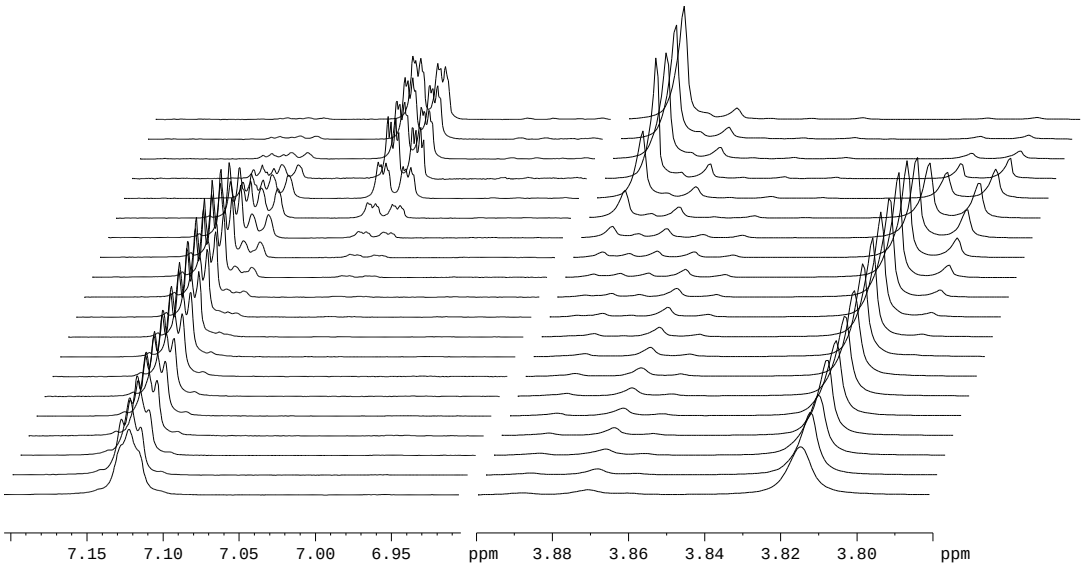
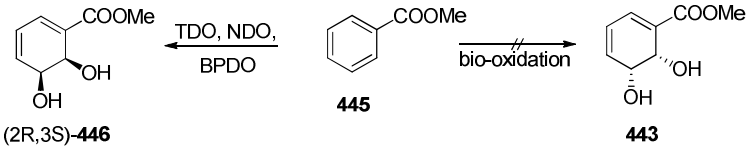


Figure 22 Dynamic NMR of iodine-mediated deprotection of **439**. Spectra are at 5 min intervals.

4.2.2 The importance of discovery

The microbial oxidation of methyl benzoate gives (2*R*,3*S*)-**446** diol in accordance with Boyd's model. In our studies, we have accessed the opposite enantiomer (2*S*,3*R*)-**443** for a first time, which is not accessible by direct bio-oxidation. (Scheme **98**)



Scheme 98 Bio-oxidation of methyl benzoate **445**

The microbial oxidation of arene diols provides only one enantiomeric series, previously this restricted the use of bio-oxidation in synthesis, but the iron rearrangement method allows the other enantiomeric series to be used for more natural products to be synthesised.

The acetonide protected *cis*-dihydrodiol metabolite **447** from methyl benzoate has been used as a synthetic precursor of carba-*β*-L-galactopyranose (**450**), carba-*β*-L-talopyranose (**448**) and carba-*α*-L-talopyranose (**449**).[284] (Figure **23**)

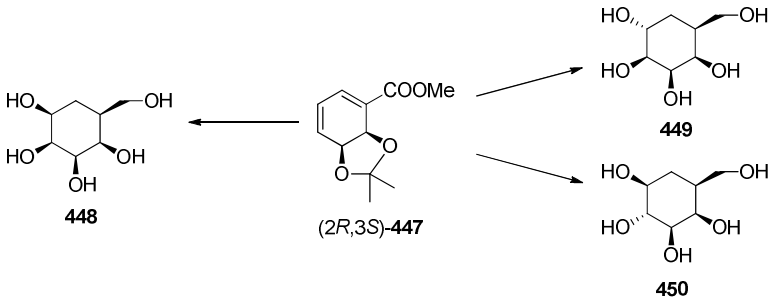


Figure 23 Variable carbasugars from methyl benzoate *cis*-dihydrodiol metabolite.

Also, further elaboration of the methyl ester will provide access to wide variety of *antipodal* arene 2,3-*cis*-diols.

4.3 Variable temperature spectra

The motivation to carry out variable temperature NMR studies was to determine whether there is a restricted tripod rotation at low temperature indicated by a split in the metal carbonyl signal in the ^{13}C NMR spectrum.

Variable temperature NMR spectra measurements were possible thanks to the use of the NMR probe, which allows experiments down to 120 K.

^{13}C-{^{1}H} NMR measurements for rearrangement product **415** did not show the $Fe(CO)_3$ carbonyl signal at approx. 210 ppm in the ^{13}C spectrum that all the other complexes exhibited. The calculations below were performed by Dr John Lowe, University of Bath.

The spectroscopic simulation shows that a very good agreement between experimental and simulated spectra of **415** was achieved (Figure **25**).

The explanation for this phenomenon is restricted rotation of the iron tricarbonyl tripod and the use of variable temperature NMR allowed us to calculate the barrier to rotation.

Usually, η^5-(cyclohexadienyl)CO_3 iron complexes show a preference for "*staggered"* geometry (Figure **24,** complexes **415a**&**c**).

Better understanding of the factors influencing the tripod orientation and knowledge of barriers to rotation is crucial to predict reactivity of metal complexes.[285,286]

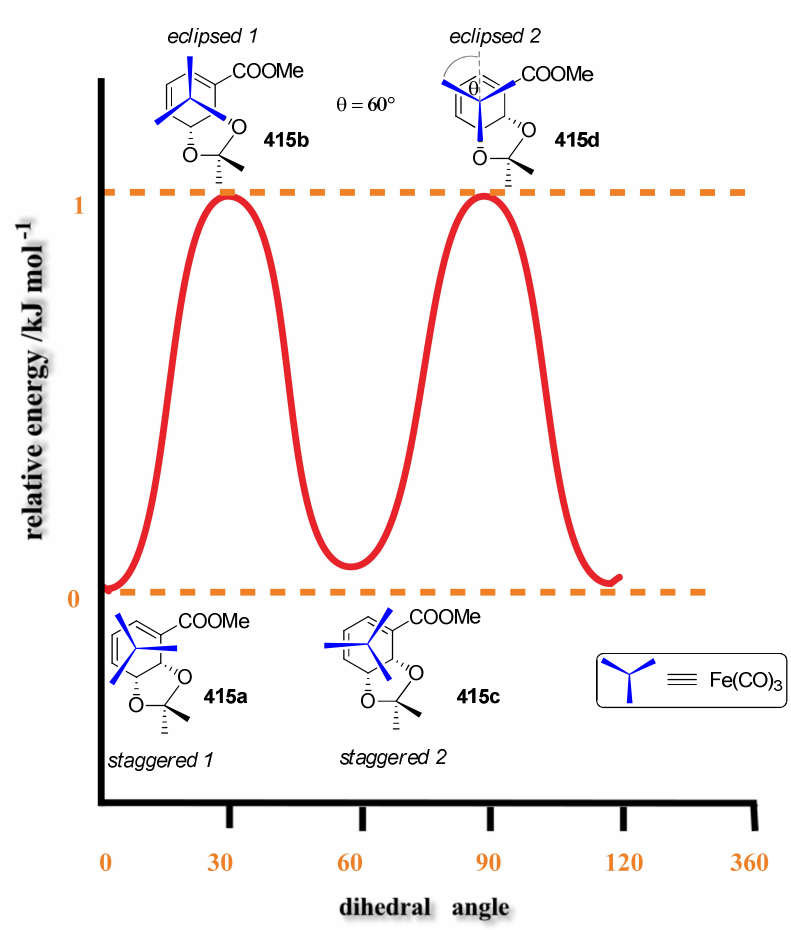


Figure 24 Possible conformations staggered and eclipsed of complex **415**

Simulations were carried out using the D–NMR program within Brüker TOPSPIN3.1, where the rate constant and, where appropriate, chemical shifts were iteratively altered until the simulated spectra gave the closest match to the real spectra. The rate constants given in Figure **25** were derived from the best fit of the simulated spectrum to the real spectrum at each temperature.

The rate constants, *k*, obtained from the simulations (Figure **25**) were used in plots (Figure **26**) of ln(*k*) versus *T* and ln (*k*/*T*) versus *T* to obtain values for the activation parameters.

Thermodynamic properties such as activation energy (E_a), entropy of activation ($\Delta S^{\ddagger}$), enthalpy of activation ($\Delta H^{\ddagger}$) and Gibbs energy of activation ($\Delta G^{\ddagger}$) were determined by Arrhenius and Eyring plots (Figure **26**) and using eqn (**1**) and (**2**)

$$\ln k = E_a/RT + \ln A \qquad \text{eqn } (1)$$

$$\ln (k/T) = -(\Delta H^{\ddagger})/RT + \ln (k_B/h) + \Delta S^{\ddagger}/R \qquad \text{eqn } (2)$$

where R = gas constant, h = Planck's constant, k_B = Boltzmann constant

The variable temperature spectra of complex **415** allowed derivation of the activation parameters for the exchange process of E_a = 46.8 ± 1.7 kJ mol^{-1}, $\Delta H^{\ddagger}_{(298)}$ = 44.4 ± 1.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −22.8 ± 5.2 J K^{-1} mol $^{-1}$ and $\Delta G^{\ddagger}_{(298)}$ = 51.2 ± 3.1 kJ mol^{-1}.

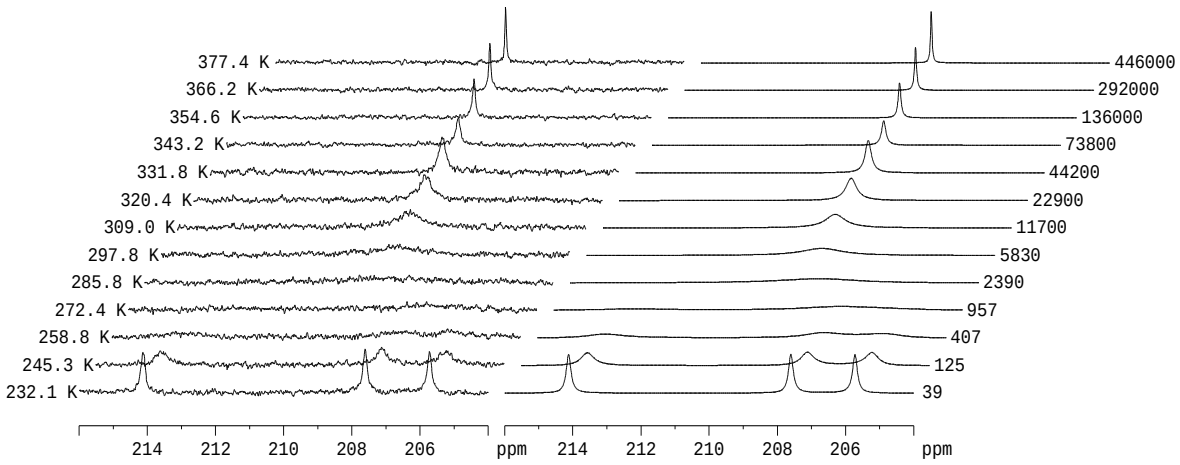


Figure 25 Experimental (*left*) and simulated (*right*) variable temperature ^{13}C-{1H} spectra of complex **415**, at 100.6 MHz in toluene-d_8, showing the iron carbonyl region only.
Rate constants (in s^{-1}) are given alongside the simulated spectra.

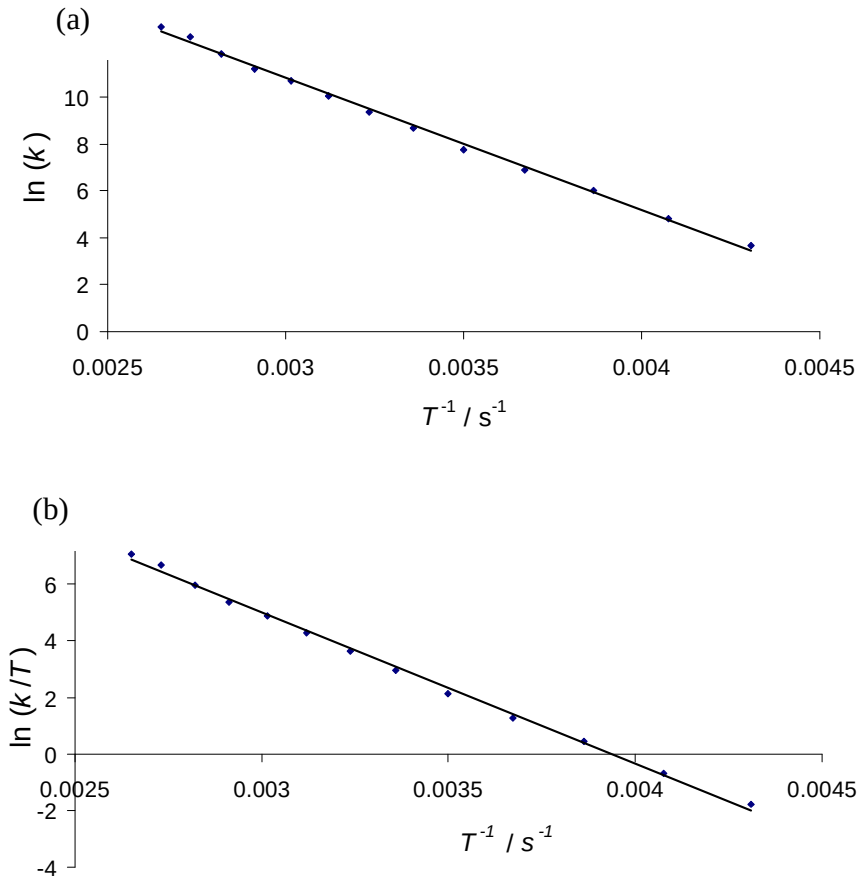


Figure 26 Plots of (a) ln (*k*) vs T^{-1} and (b) ln (*k*/T) vs T^{-1} for the carbonyl exchange in complex **415.**

4.4 Conclusions

The present study has primarily led to a novel rearrangement product in very high *e.e*. From labelling studies it appears that formation of this product is through acetonide migration rather than methyl ester group migration. We have proposed a plausible mechanism of formation of this product. Understanding this process is of high importance in cyclohexadiene iron complex chemistry, and will answer an important question about diversity of the novel rearrangement.

As an application of this methodology we are able to access arene 2,3-diol derivatives of non natural configuration not obtainable by bio-oxidation.

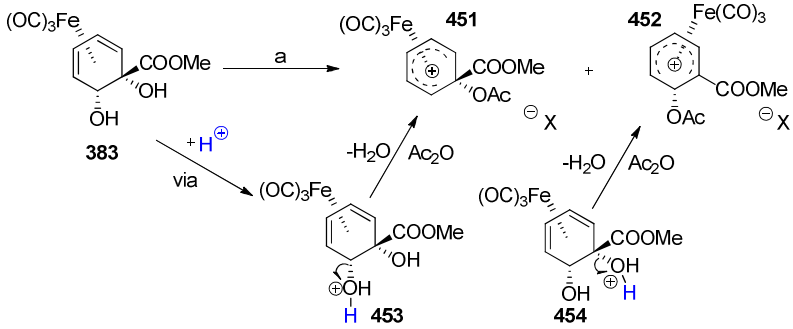
Some of the results presented in this Chapter were published as a paper in *Chemical Communications.*[52]

Chapter 5
Nucleophilic addition

CHAPTER 5: NUCLEOPHILIC ADDITION

5.1 Optimisation of Cationic products formation

Whilst examining synthetic routes to cationic η^5 products from iron tricarbonyl complex **383**, it was noted that the reaction of iron tricarbonyl complex **383** in acetic anhydride in the presence of tetrafluoroboric acid-diethyl etherate stood out as a potentially useful protocol from which a general methodology could be developed. This method for the preparation of cationic iron complexes, was previously established by Pearson *et al*. with HBF_4 in acetic anhydride. The acetic anhydride plays three roles. Not only is it the solvent, but it also serves to acetylate the alcohol function groups *in situ*, as it has been shown that η^5 cyclohexadienyl complexes that have an unprotected alcohol rapidly decompose by aromatisation.[256] Finally, the acetic anhydride acts as a desiccant, removing the water formed upon dehydroxylation of the complex as well as any water present in the added acid.



Scheme 99 Preparation of cationic complexes **451** and **452**

Reagents and conditions: (a) HX (X = $^{\ominus}BF_4$, $^{\ominus}PF_6$, $^{\ominus}OTf$) (10.0 equiv.), Ac_2O, −10 ℃, 1h, N_2.

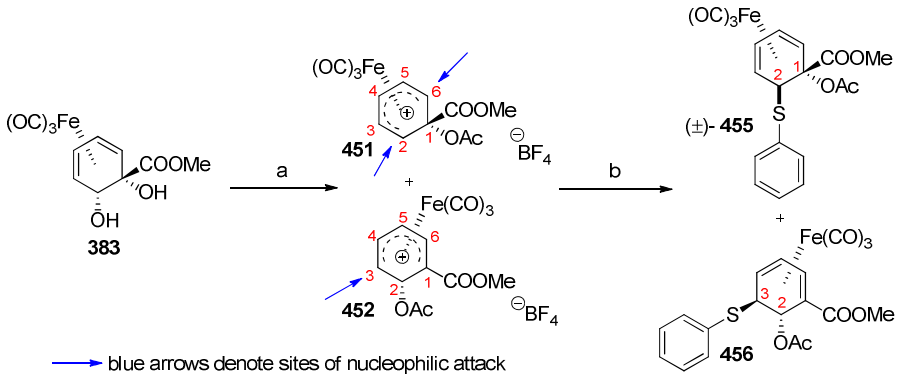
A proposed mechanism for the reaction is outlined below (Scheme **99**). The first stage involves protonation of hydroxyl groups by the acidic species, to form cationic intermediates **453** and **454**. Subsequent elimination of water and

acetylation yielded the two acetylated intermediates. Water free work up resulted in the isolation of products **451** and **452**, which in turn were found to be very reactive in the presence of nucleophiles.

Originally we had attempted formation of the cationic η^5 iron salts using a known procedure, triflic acid in DCM, but to no avail. Treatment of complex **383** with triflic acid in a more polar solvent such as MeCN, followed by treatment with aqueous 1M NaOH provided disappointing results, as mostly SM was recovered. Work up and purification failed to isolate the desired product.

It seemed that the solvent was an important key factor for the preparation of the stable iron intermediate. We proposed that this problem might be surmounted by acetylation of the hydroxyl group by simply running the reaction in acetic anhydride at −10 ℃ followed by addition of acid HX (X = $^{\ominus}BF_4$, $^{\ominus}PF_6$, $^{\ominus}OTf$, $CF_3CO_2^{\ominus}$).

At this point we saw the potential for the incorporation of nucleophiles within this route. We envisaged that if successful with a range of chosen nucleophiles, the scope of this reaction could be extended further in order to produce a range of functionalized cyclohexadiene derivatives. This iron-mediated diene rearrangement would represent a new route to dihydroarene 2-*cis*, 3-*trans* derivatives not possible to access via direct bio-oxidation. A vast array of nucleophiles can be envisioned such as C, O, N, P, S or H.[287]
The reactivity of these salts towards nucleophiles was examined during my work.



Scheme 100 Formation of thiophenolate adducts

Reagents and conditions: (a) Acid (TFA, HOTf, HPF_6, HBF_4, $HBF_4{\cdot}(OEt)_2$) (10.0 equiv.), Ac_2O, −10 °C, 1 h; (b) NaSPh (4.28 equiv.), THF or MeCN, Ac_2O, 0 ℃, 1 h.

In order to optimise conditions for the addition reaction, the representative nucleophile (NaSPh) was chosen, with which we have tried many different conditions.

A wide range of conditions were studied in order to optimise the reaction of cationic salt formation, and these are summarised in Table **3** below. Consequently, several experiments were conducted using a variety of acids and solvents. This helped to determine whether the acid had a significant role to play in terms of yield during formation of cationic salts.

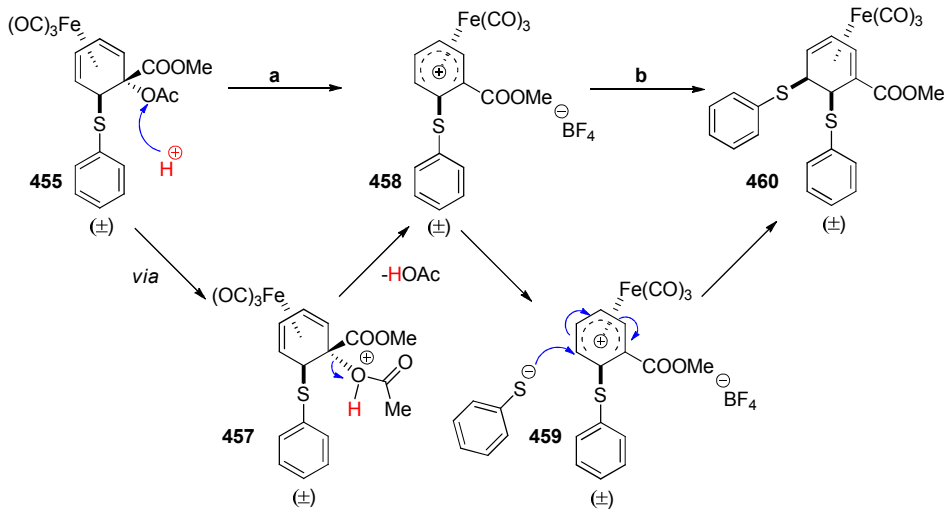
The equivalents a sodium thiophenolate (~4.28 equiv.) and acid was held constant, while a range of solvents were investigated at the same temperature (−10 ℃) over and the same reaction time (1 h).

Table 3 10.0 eq. acid, Ac_2O, –10 ℃, 1 h, then precipitation, filtration, sol vation in alternative solvent, 4.3 eq. NaSPh, 0 ℃, 1 h. [*] 8% of a byproduct **470** was also obtained.

Entry	acid	Solvent for step b	Yield of (±)-465 (%)	Yield of 466 (%)
1	TFA	THF	25	4
2	TFA	MeCN	20	3
3	TFA	Ac_2O	-	
4	HOTf	THF	36	3
5	HOTf	MeCN	38	6
6	HOTf	Ac_2O	-	
7*	HPF_6	THF	45	6

8	HPF_6	MeCN	23		0
9	HPF_6	Ac_2O		-	
10	HBF_4	THF	14		4
11	HBF_4	MeCN	13		5
12	HBF_4	Ac_2O		-	
13	$HBF_4.OEt_2$	THF	57		0
14	$HBF_4.OEt_2$	MeCN	34		0
15	$HBF_4.OEt_2$	Ac_2O		-	

As will be seen, this study was not without surprises. The reaction with hexafluorophosphoric acid, followed by nucleophilic addition of sodium thiophenolate in THF, did not proceed cleanly and gave two products **455** and **456** in 45% and 6% respectively (Entry 7). These yields were slightly lower than those obtained with HBF_4-ether (Entry 13). Uniquely with HPF_6 the formation of second nucleophilic product was noticed **460**. The explanation of this result is an involvement of a novel cationic intermediate **458**, which subsequently underwent nucleophilic addition with sodium thiophenolate giving a novel product **460**, in 8% yield, scheme **101**. (*Vide infra*)



Scheme 101 Formation of product **460.**

Reagents and conditions: (a) HPF_6 (10.0 equiv.), Ac_2O, −10 °C, 1 h; (b) NaSPh (4.28 equiv.), THF, 0 ℃, 1 h.

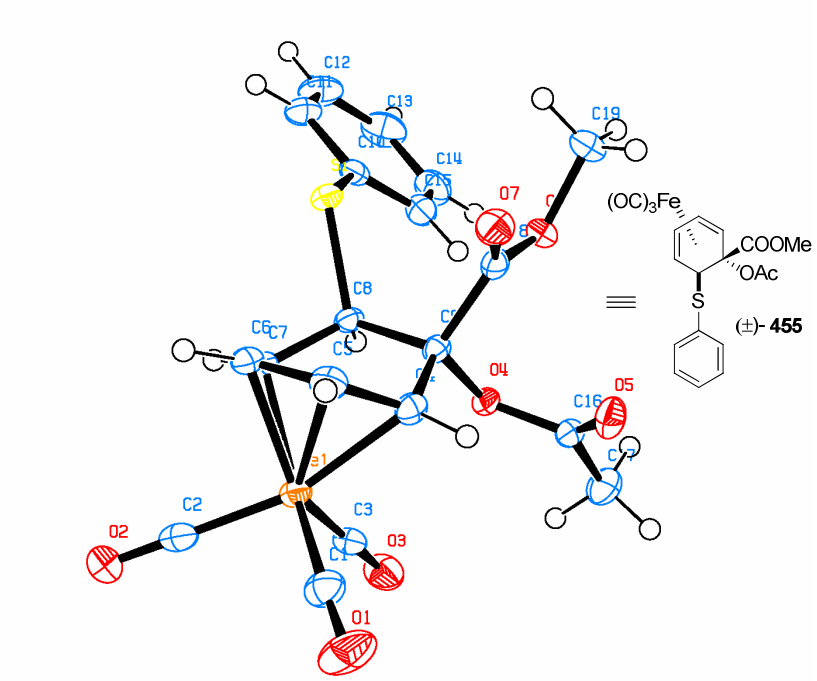


Figure 27 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **455.**

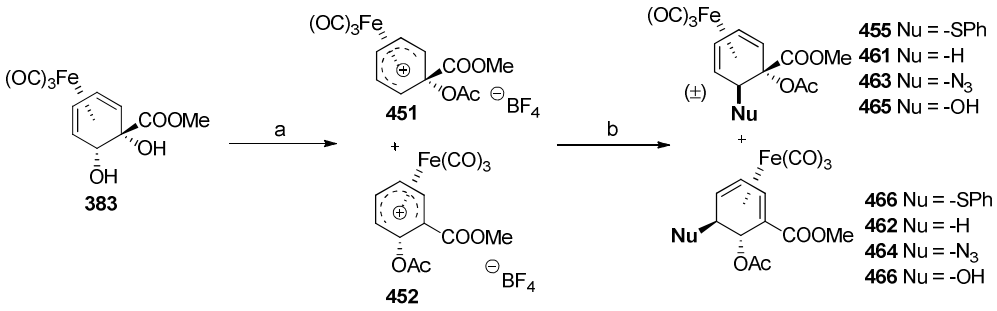
We concluded from these studies, that the most effective conditions were with tetrafluoroboric acid diethyl etherate and in THF. At this stage, we optimised the work up conditions for this reaction by several recrystallisations with TBME and cold diethyl ether.

Having developed a set of successful conditions for formation and isolation of the cations, we looked to expand the scope of the methodology by exploring the addition of diverse nucleophiles

5.2 Nucleophilic addition reactions

The results for a mixture of cationic intermediates **451** and **452**, shown in Table **3**, indicate a general preference for nucleophile addition to C-2/C-6 and C-3, respectively. During our initial attempts to form addition products, several

solvents were studied. However, only acetonitrile or the mixture 2:1 in THF were found to give promising results. Moreover, we found that the reaction is not dependent on the amount of acid used. Subsequent experiments demonstrated that varying the amount of HBF_4–ether from 10.0 equivalents to 4.0 equivalents resulted in the same addition products in the same yields.



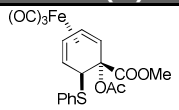
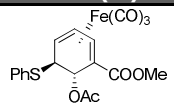
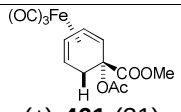
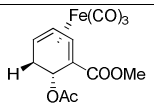
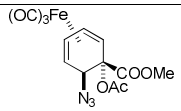
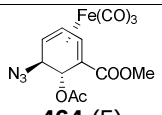
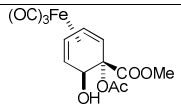
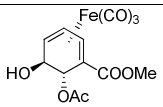
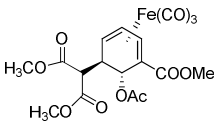
Scheme 102 Synthesis of wide variety of nucleophilic addition products.
Reagents and conditions: (a) $HBF_4{\cdot}(OEt)_2$ (10.0 equiv.), Ac_2O, −10 °C, 1 h; (b) $Nu^{\ominus}$ (5.00 equiv.) THF or MeCN, 0 ℃, 1 h.

In general, the attack of nucleophilic species proceeded in high yields and takes place regioselectively, at the terminus of the co-ordinated dienyl system (Davies–Green–Mingos rules)[288] and also stereoselectively *anti* to the tricarbonyliron fragment.[288]

Based on the established stereo- and regioselectivity, we also invoked several other reagents for nucleophilic addition to these cationic intermediates.

The first step reactions were carried out for 1 hr in acetic anhydride, which after work up gave a mixture of cationic intermediates which subsequently, underwent nucleophilic addition, and it was found that, the yields varied for the different nucleophilic species.

Table 4 Reactivities of diverse nucleophiles towards cations **451** and **452.**

Entry	Nucleophile	Product from 451 Yield (%)	Product from 452 Yield(%)
1	NaSPh [B]	 (±)-**455** (45)	 **456** (6)
2	$NaBH_4$ [A]	 (±)-**461** (31)	 **462** (4)
3	NaN_3 [A]	 (±)-**463** (34)	 **464** (5)
4	0.1M NaOH [A]	 (±)-**465** (25)	 **466** (10)
5	*n*-BuLi, $CH_3CO_2CH_2CO_2CH_3$ [C]	-	 **467** (12)

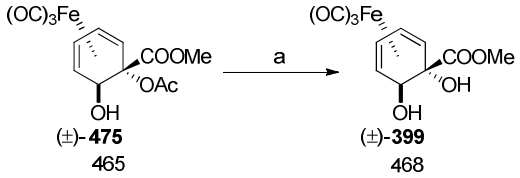
Condition A: CH_3CN, 0 °C→rt, 1 h
Condition B: THF, −78 °C→rt, 1 h
Condition C: THF (10 mL) CH_3CN (0.5 mL), 1 h

The most noteworthy observation is that the reaction with PhSNa and $NaBH_4$ which gave **(±)-455** (45%) and **(±)-461** (31%), respectively showing an improved yield (Entry 2). Reactions using lithiated dimethyl malonate gave the poorest results (Entry 5). Several attempts were conducted to obtain (±)-*trans*-diol **465**. Addition of 0.1M solution of sodium hydroxide to a mixture of cationic iron tricarbonyl complexes in acetonitrile induced formation of desired products, which were isolated as **(±)-465** and **466** in 25%, and 10%, respectively (Entry 4). It was intended that this route would furnish *trans*-addition products in better overall

yield. After several attempts, we were unable to improve the yields for those reactions.

Lowering the amount of acid and/or increasing the equivalents of the nucleophilic species had no effect on the reaction.

We were pleased that the deacetylation stage of the reaction with sodium methoxide was found to have gone to completion after reaction time of 24 h at ambient temperature yielding product **468**, Scheme **103**.



(±)-**475** (±)-**399**

465 468

Scheme 103 Deacetylation of **(±)-465**

Reagents and conditions: (a) NaOMe (20.00 equiv.) MeOH, 24 h, rt, (quantitative).

The structure of (±)-**461**, and (±)-**468**, were further confirmed by X-ray crystallography. (Appendix **1**)

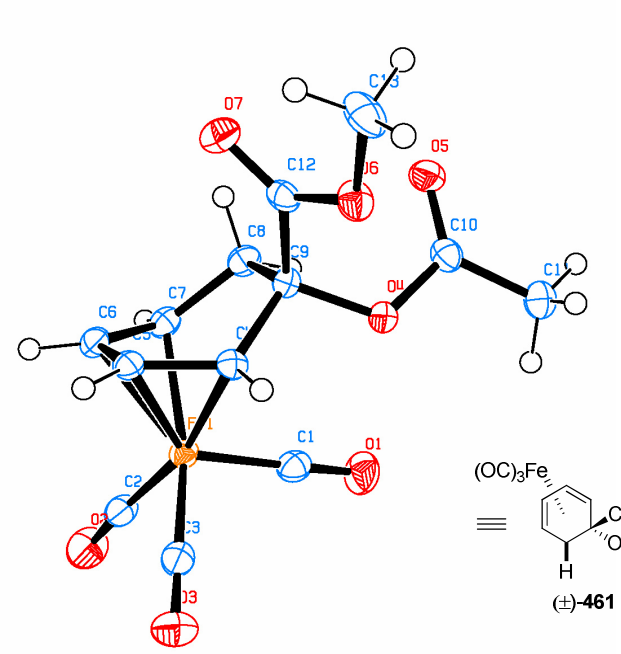


Figure 28 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **(±)-461.**

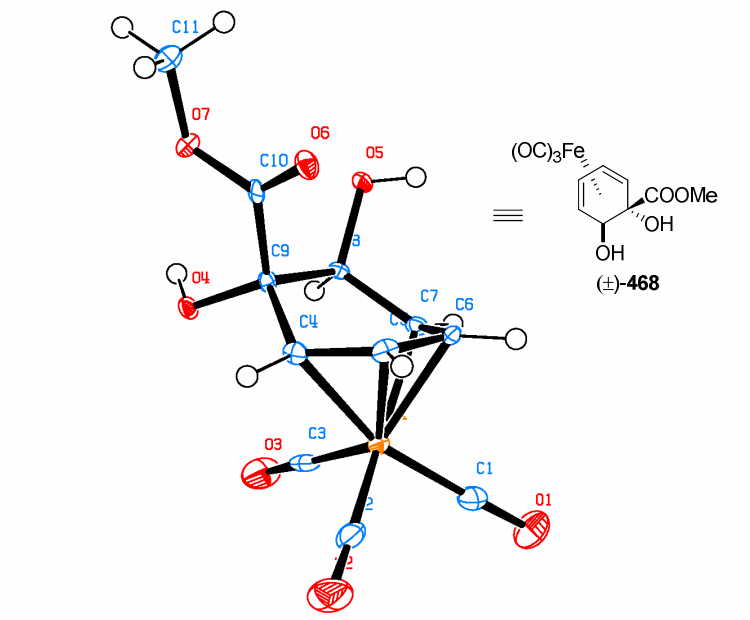
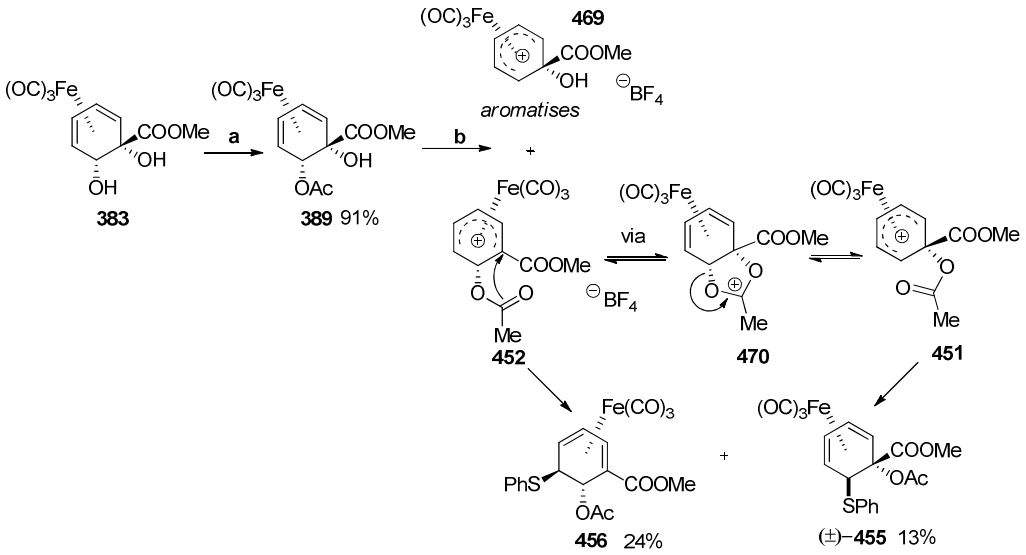


Figure 29 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **(±)-468.**

The overall yields after two steps in some entries were not high enough for addition reactions towards cationic salts. We therefore set out to develop an approach to the efficient and stereocontrolled synthesis of iron complexes, without isolations of salts, Scheme **104**.



Scheme 104

Reagents and conditions: (a) pyridine, −10 ℃ for 1 h, then rt for 18 h, (91%); (b) HBF_4–ether, THF, −10 ℃, 1 h, PhSNa, −78 ℃, 1 h.

In order to be able to modify and improve the synthesis of the nucleophilic addition products, it was imperative that we thoroughly understood this reaction. Here, an alternative synthetic approach towards nucleophilic addition products has been examined. This acetylation of the hydroxy group was completed at C-2 only giving product **389**, which was subsequently treated with the acid without any acetic anhydride. Surprisingly two nucleophilic addition products **455** and **456** were delivered in 13% and 24% yield respectively.

One likely explanation which would account for this observation involves reversible reaction of acetylation at C*2* position of **452**. Consequently, the release of favourable and more stable product **451** is observed, which was reacted further with sodium thiophenolate to give **455**, Scheme **104**.

5.3 Details of NMR studies

We have investigated further the reaction with acid in order to explore the possible pathway and mechanism of this reaction. The reaction conditions employed used compound **383**, HBF_4-etherate (50 µL) in acetic anhydride at room temperature. The reaction was monitored by ^{1}H–NMR, and the change in integration of various resonances was observed. Interestingly, ^{1}H–NMR spectroscopic analysis showed that the mixture of products had been formed as **451** and **452** in a 3:1 ratio in 1 h.

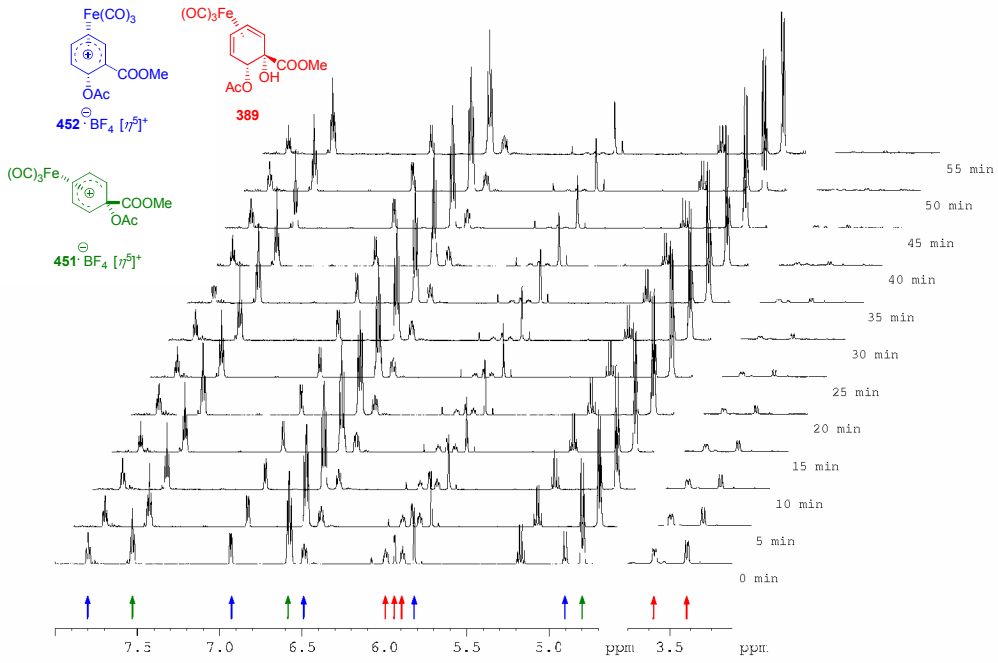


Figure 30 ^{1}H-NMR stacked spectra showing real-time formation of **451** and **452.**
Spectra acquired at 5 minute intervals in Ac_2O, 5 eq. $HBF_4{\cdot}OEt_2$, 298 K, employing solvent suppression.

Surprisingly after prolonged time, the ratio of cationic product **451** possessing C_2 symmetry plane drastically increased whereas the level of product **452** become very low. The explanation of this phenomenon could be drawn based on the better stability of **451** since the electron withdrawing ester is not conjugated to the electron-deficient π-system, whereas the cationic complex **452** is destabilised by conjugation to the ester. The formation of kinetically stable product **451** shifts the equilibrium to the right. Figure **31**

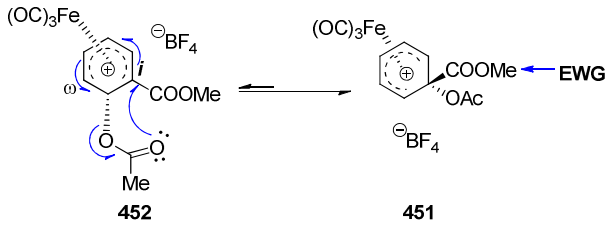
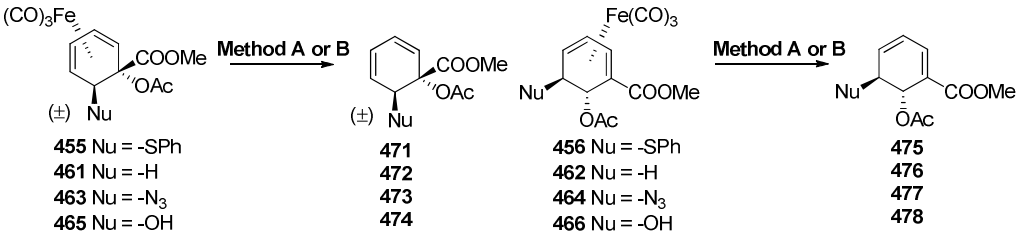


Figure 31 Double effect of stabilisation of symmetrical product **452.**

The presence of activating (-OAc) and deactivating group (-COOMe) on the same carbon atom (C1) can stabilized positive charge in the cyclohexadienyl ring system more effectively due to breaking down the conjugation between methyl ester group and diene.

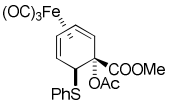
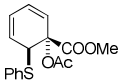
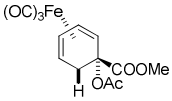
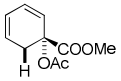
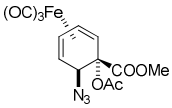
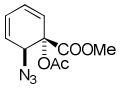
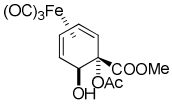
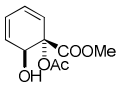
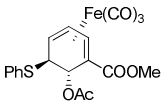
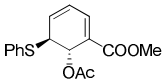
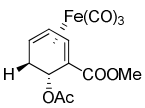
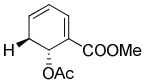
5.4 Demetallation of novel cyclohexadiene iron complexes.

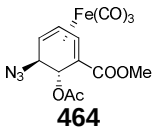
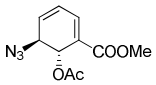
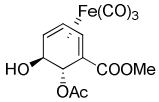
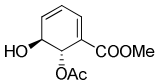
In order to demonstrate the potential applications of this chemistry in organic synthesis, demetallated compounds must be readily available. Two particular demetallation procedures have been used. The reaction with anhydrous trimethylamine *N*-oxide in benzene (**Method A**) was less effective than the reaction with ceric ammonium nitrate in acetone (**Method B**), Scheme **105**, Table **5**



Scheme 105 Demetallation of complexes with CAN and TMANO.

Table 5 Demetallation of iron complexes with CAN and TMANO

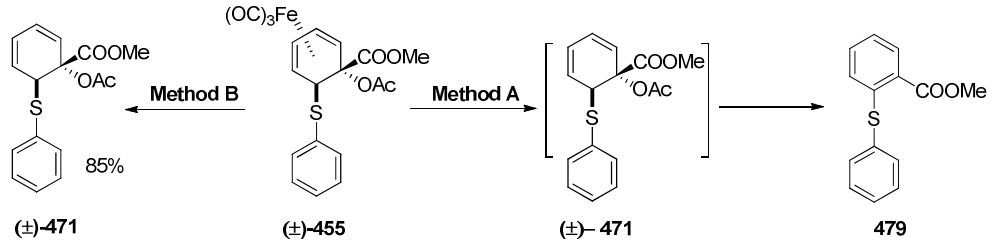
Entry	Substrate	Product Method A Yield %	Product Method B Yield %
1	 (±)-**455**	0	 (±)-**471** 85
2	 (±)-**461**	-	 (±)-**472** 0
3	 (±)-**463**	31	 (±)-**473** 64
4	 (±)-**465**	22	 (±)-**474** 100
	Complex 2,3		
5	 **456**	-	 **475** 91
6	 **462**	-	 **476** 63

7	 **464**	-	 **477** 63
8	 **466**	-	 **478** 53

Method A: Me_3NO, 36.00 equiv., dry benzene, rt, 24 h
Method B: (1) $(NH_4)_2Ce(NO_3)_6$, 3.00 equiv., acetone, 0 ℃, 5 min, rt, 25 min (Entry 4), 3 h (Entry 7), 4 h (Entry 3), 50 min (Entry 6)
"-" reaction not performed at all.

In some cases after removing iron tricarbonyl moiety with TMANO from cyclohexadiene ring system, some aromatics were detected along with a rather complex mixture of products (Entry 1, Method A and Entry 2, Method B). In order to establish the viability of detachment of the metal from the tricarbonyl(η^4-cyclohexadiene)iron complex, the adduct (±)-**455** was converted to the aromatic derivative **479** using Me_3NO for 24 h in benzene, Scheme **106**.

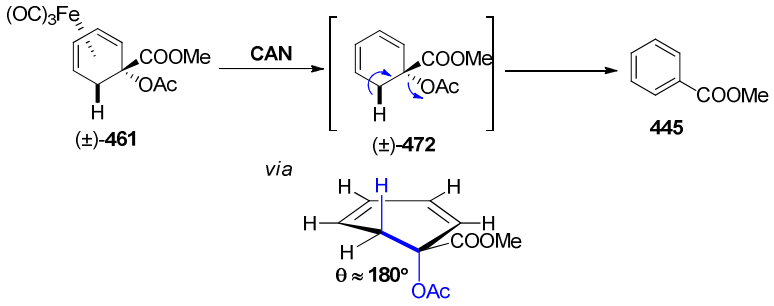
Demetallation of (±)-**455** gave desired product, but solutions slowly decompose in the presence of air. Successfully demetallation of the adduct (±)-**455** gave derivative (±)-**471** in 85% yield using CAN for 15 min in acetone (Entry 1, Method B).



Scheme 106 Demetallation of iron complex **455.**

Gratifyingly, demetallation of azide (±)-**463** with CAN preceeded uneventfully providing (±)-**473** in 64% yield, (Entry 7). However, no improvement in yield was forthcoming after several conducted attempts.

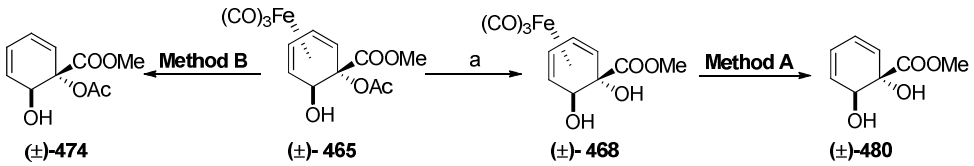
Hydride product (±)-**472** was also synthesized (Entry 2), although only this ligand undergoes E_2 elimination, where two hydrogen atoms are removed from adjacent carbon atoms ($\theta \approx 180°$) proved difficult to isolate it after silica gel column chromatography. This result could potentially be explained by the protonation of the acetylated group and formation of aromatic product after the *trans*-elimination step, Scheme **107**.



Scheme 107 Formation of hydride product **(±)-472**

We had already demonstrated that demetallation of novel iron complexes was productive. (Table **5**) However, in our hands when the reaction was attempted with 1,2-hydride iron complex (±)-**461** with TMANO, this unfortunately failed, resulting in complete loss of material.

The synthesis on a very small scale (~5mg) of novel *trans*-diol **480** was accomplished in two steps from (±)-**465**, after reaction with sodium methoxide (20.00 equiv.) in MeOH for 24 hr, further purified and treated with CAN in acetone for 25 min, furnished the desired product (±)-**480** however it proved to be unstable on a silica gel, Scheme **108**.



Scheme 108 Formation of (±)-*trans*-diol **480**

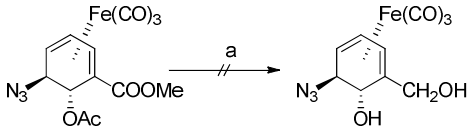
Reagents and conditions: (a) NaOMe (20.00 equiv.), MeOH, N_2, 24 h, rt, (quantitative).

5.5 Determination of e.e.

All racemic (**455, 461, 463, 465**) iron complexes were examined on a chiral HPLC column packed with Chiracel OD using Hex:IPA (95/5) as eluent. Attempted resolution of the rearrangement nucleophilic addition (**456, 462, 464, 466**) products using the same conditions as above showed a single peak in each case.

However, in the absence of racemic material for comparison, we could not exclude the possibility that enantiomers were co-eluting, unlikely though this seemed given that baseline separation was achieved for all the structurally similar racemic "1,2" adducts.

To further investigate the enantiopurity of the "2,3" products, we decided to employ a procedure reported by Bull and James, which utilises a simple three component chiral derivatisation to allow determination of *e.e.* by ^{1}H–NMR spectroscopic analysis.[289-295] This procedure works for both amines and for diols. Thus, several attempts to reduce 2,3-azide complex **464** were carried out with DIBAL-H, but were unproductive, giving a complex mixture of inseparable products.

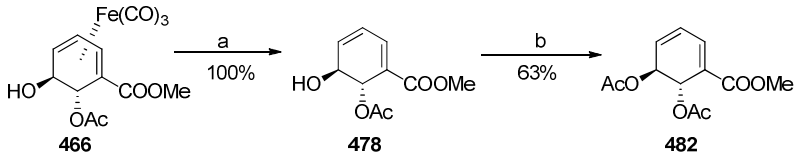


Scheme 109 Attempted reduction of iron complex **464.**

Reagents and conditions: (a) DIBAL-H (7.00 equiv.), THF, −78 ℃ →rt, 24 h.

Faced with this setback, we turned back to the literature to see if racemic syntheses had been reported for any of the “2,3” adducts or their demetallated derivatives. In fact these were all previously unreported. However, a derivative (peracetate) was known: **(±)-482** which is an excellent reference point for our iron complexes, and after employing it on chiral stationery phase, this could provide further a value for the enantiopurity of the “2,3” rearrangement products.

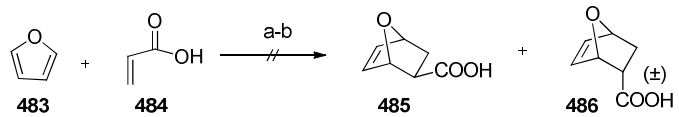
In order to verify this, it was decided to apply compound **478** after further protection of hydroxyl group. This product was examined later by CHIRALCEL® OD–I column Scheme **110**, Figure **32**.



Scheme 110 Synthesis of peracetate **482**

Reagents and conditions: (a) $(NH_4)_2Ce(NO_3)_6$, 3.00 equiv., acetone, 0 ℃, 5 min, rt, 25 min; (b) Ac_2O, (2.20 equiv.), DCM, Et_3N, 0 ℃ →rt, 24 h.

When **478** was treated with acetic anhydride (2.20 equiv.) in DCM, followed by Et_3N peracetate **482** was obtained in 63% yield. The reaction appeared to be sluggish and several portions of Ac_2O were required to drive the reaction to completion.

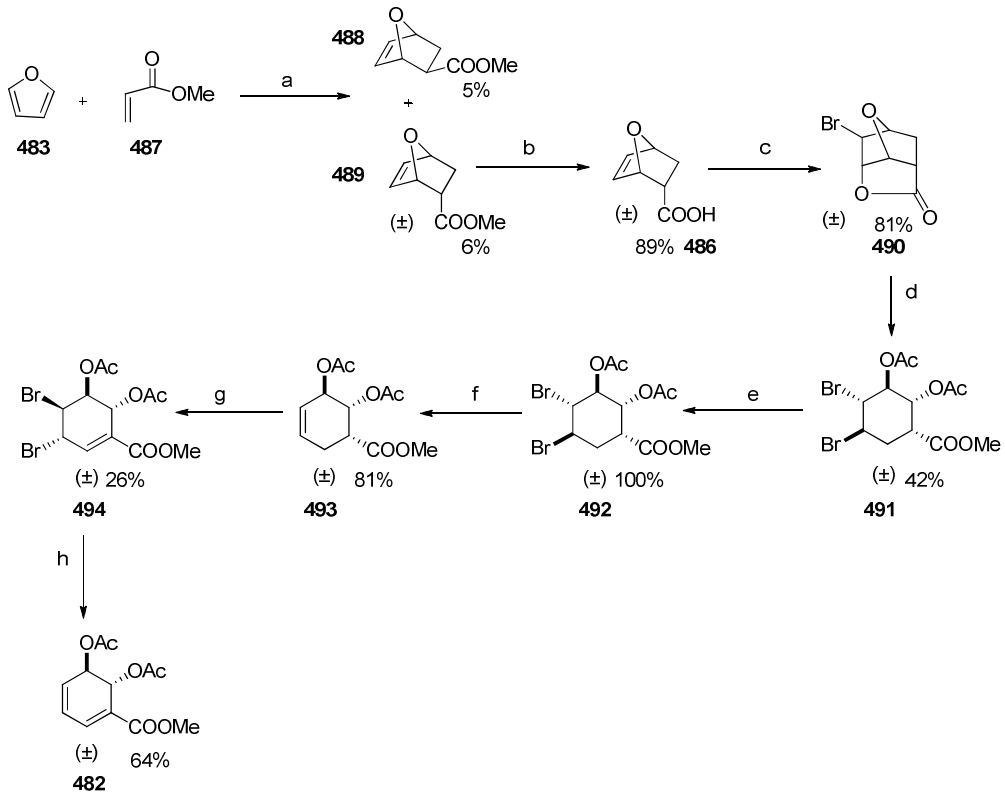


Scheme 111 Attempted Diels-Alder reaction between furan and acrylic acid

Reagents and conditions: (a) BH_3–THF (0.01 equiv.) over 30 min, 2 ℃, 18 h, (b) hydroquinone (0.01 equiv.) over 30 min, 2 ℃, 75 d.

To access the corresponding racemate (±)-**482** by independent synthesis initially we attempted the conditions reported by Suami *et al.* for the Diels–Alder reaction using commercially available furan **483**, and acrylic acid **484**,[296] Scheme **111**. Despite exploring several cycloaddition reactions the adduct **486** was not obtained directly from acrylic acid. For example, a neat mixture of acrylic acid and furan with added hydroquinone, after 75 days (as reported!) gave a complex mixture, as did the catalysed reaction with BH_3−THF which gave a mixture of starting materials. We speculate that HOMO−LUMO interactions and reagent purity are at least partially responsible for the difficulties associated with this reaction. The failure of acrylic acid to undergo clean cycloaddition as reported led us to search for an alternate route.

Thus we decided to attempt to carry out a similar reaction starting with methyl acrylate **487** instead, following a procedure published by Kotsuki *et al*.[297] Although, the cycloaddition was not completely satisfactory, sufficient amounts of (±)-**489** were obtained to attempt the hydrolysis, Scheme **112**.



Scheme 112 Ogawa's synthesis of **(±)-482**

Reagents and conditions: (a) $BH_3{\cdot}OEt_2$ (0.1 equiv.) over 30 min, −20 °C, 18 h; (b) 1 M NaOH, 23 h, rt; (c) Br_2, $NaHCO_3/H_2O$, 1 h; (d) HBr, HOAc, 2 days, 80 ℃; (e) $TMSCHN_2$, MeOH:Benzene (1:1); (f) Zn (powder), AcOH, 1 h, 70 ℃; (g) NBS (2.00 equiv.) AIBN, CCl_4, reflux, 2 h; (h) Zn (powder, 4.00 equiv.), AcOH, 2.5 h.

The target Diels–Alder products **488** and **489** were obtained from commercially available furan and methyl acrylate when treated with the Lewis acid $BH_3{\cdot}OEt_2$ (0.1 equiv) at −20 ℃ for 18 h, and after silica gel chromatography led to (±)-**489**, albeit in low yield 6%.

Upon treatment of (±)-**489** with 1M NaOH at ambient temperature the free acid (±)-**486** was obtained in 89% yield.[298]

The acid (±)-**486** was treated with bromine in $NaHCO_3/H_2O$ and stirred for 1 h, and after recrystallisation afforded the bromolactone (±)-**490** in 81% yield[299] Scheme **112**.

Reacting (±)-**490** in a sealed tube at 80 ℃ with 33% hydrogen bromide and glacial acetic acid for 2 days afforded (±)-**491** in 42%.[300] Then (±)-**491** was subjected to a esterification reaction using (trimethylsilyl)diazomethane (2.0 M solution in hexanes) to furnish (±)-**492** in quantitative yield. Analytical data agreed with literature values. This product (±)-**492** was easily converted into (±)-**493** in 81%, using zinc powder and acetic acid at 70 ℃ for 1 h. Further conversion to the dibromide (±)-**494** was attempted using a mixture of (±)-**493**, and NBS (2.00 equiv.) in the presence of substoichiometric amount of AIBN in CCl_4, at reflux temperature for 2 h resulted in formation of a major compound (±)-**494** along with many other bromides, but after purification by chromatography on silica gel it was isolated in 26% yield[301] Scheme **112**.

With (±)-**494** now available, the debromination reaction was attempted employing zinc powder (4.00 equiv.) in AcOH which lead to the final racemic diene (±)-**482** in 64%. Intriguingly, the reaction was completed in 2.5 h at room temperature as monitored by TLC, whereas only 10 min was required for zinc dust according to the literature procedure.[300]

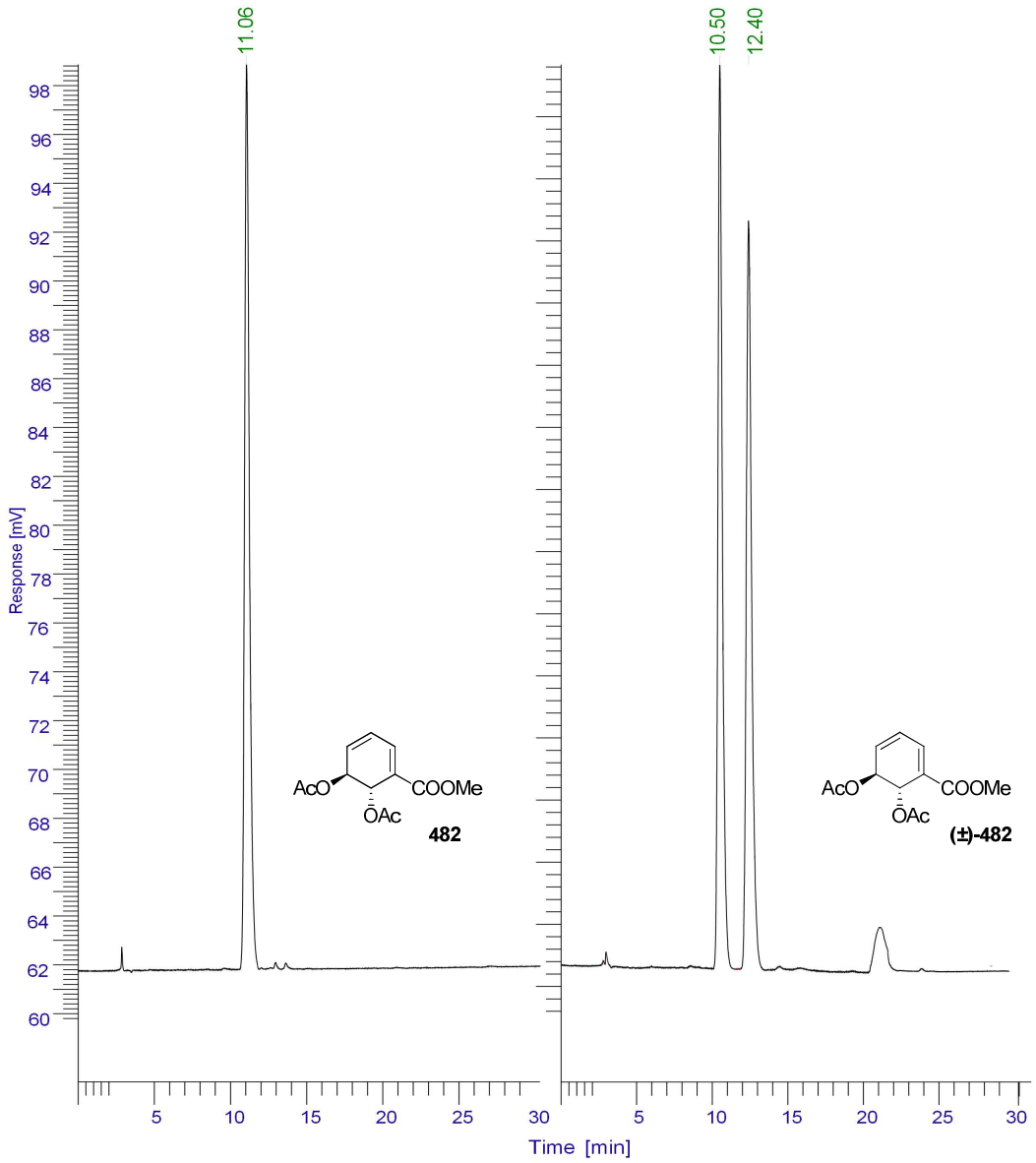


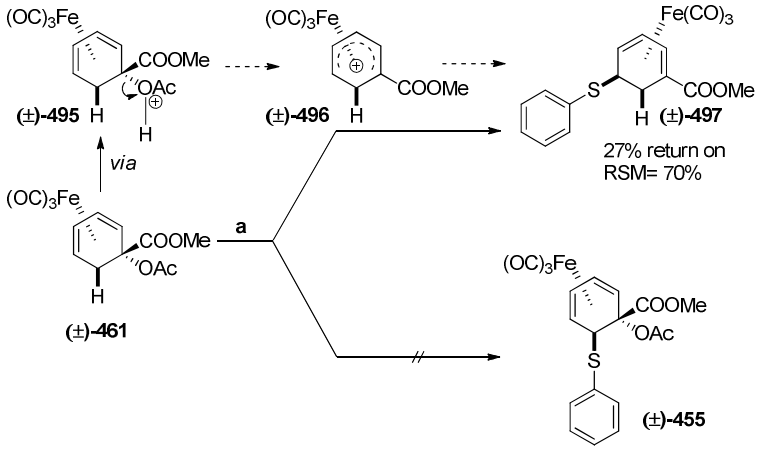
Figure 32 Chromatograms for **452**

HPLC: CHIRALCEL® OD–I column, Hex:IPA = 95/5, 1.0 mL/min., λ = 254 nm, t_{R1} = 10.50 min (11.06 min), t_{R2} = 12.40 min

The key finding: the material produced by the iron route is >99% *e.e.* and therefore the “2,3” products are enantiopure.

5.6 The scope of second nucleophilic additions

Next we began our studies on a possible *second* nucleophilic addition reaction on (±)-**461** by addition of trityl tetrafluoroborate followed by treatment with acetic acid , gave a cationic intermediate which reacted with PhSNa, Scheme **113**.
Intriguingly novel iron complex (±)-**497** was isolated in low yield (27%). The formation of (±)-**497** could be explained on the basis of the bulky trityl cation effecting deacetoxylation instead of hydride abstraction. This implied formation of η^5-cyclohexadiene intermediate (±)-**496** followed by the nucleophilic addition of PhSNa and concomitant rearrangement gave product (±)-**497** however in poor yield.



Scheme 113 Synthesis of second nucleophilic addition product **(±)-497**
Reagents and conditions: (a) CPh_3BF_4, (1.05 equiv.), DCM, rt, 1 h, then HOAc (1.00 equiv.), −12 ℃, 1 h, PhSNa (2.00 equiv.), 0 ℃, 1 h.

Encouraged by the results obtained using tricarbonyl complex (±)-**461,** which demonstrated the viability of a second nucleophile addition, we wished to extend the scope of this methodology to an ethyl ester complex, as this would allow us

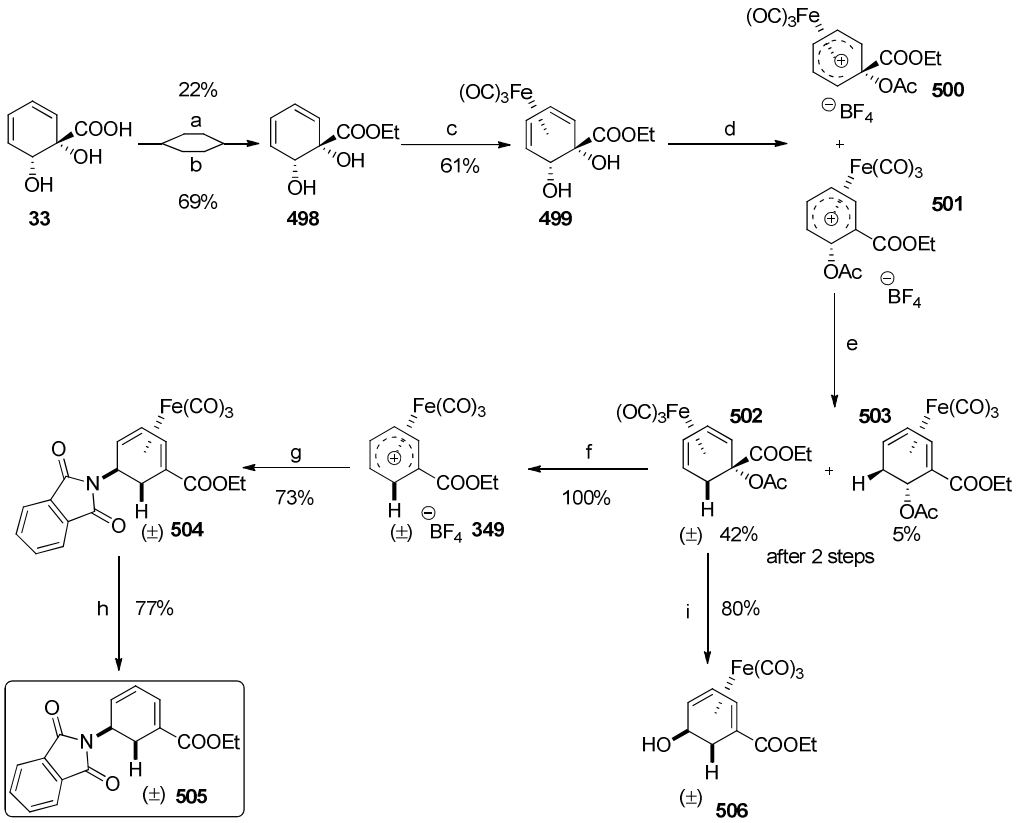
to demonstrate the usefulness of this methodology by the preparation of oseltamivir intermediates.

5.6.1 Oseltamivir intermediates

The practical industrial routes for the synthesis of oseltamivir were developed by F.Hoffman-La Roche Ltd. and Gilead Sciences, Inc, which are still in use today. The major starting material according to Roche in oseltamivir production is shikimic acid. It was originally derived from star anise, an herb grown in China and Vietnam. Innovation in oseltamivir synthesis could further drive down prices. While current demand for seasonal influenza treatment and pandemic stockpiling are being met, it is important to find an alternative way to have secure supply of oseltamivir.

There are many researchers interested in syntheses of Tamiflu.[302] Several groups have made oseltamivir from an arene diol (Hudlický[75,303,304,305,] Banwell[306,307], Fang[308]) but nobody has reported the use of 1,2-*cis* microbial diol **33** in its synthesis.

We wanted to develop methodology which used starting materials which are cheap and readily available, thus benzoic acid could be a possible choice. It was clear that the use of a micriobial derivied diol **33** could lead to iron carbonyl intermediate salt **349** after esterification, complexation and dehydroxylation, all using well known procedures developed in our lab, scheme **114**.



Scheme 114 Synthesis of Trost's key intermediate (±)-**505**

Reagents and conditions: (a) EtI (1.10 equiv.) Et_3N (1.10 equiv.) acetone, rt, 24 h; (b) CsF (1.5 equiv.) DMF, EtI, N_2, rt, 23 h; (c) $Fe_2(CO)_9$, THF, 5 d, rt, argon, (61%); (d) + (e) HBF_4·ether (10.00 equiv.), Ac_2O, −10 ℃, 1 h, then $NaBH_4$ (5.00 equiv.) 0 ℃, 1 h, CH_3CN; (f) HBF_4·ether (1.50 equiv), DCM, −12 °C, 1 h; (g) Potassium phthalimide (3.00 equiv.), DCM, 0 ℃, DIPEA (1.10 equiv.), 30 min at 0 ℃ →rt, 1 h; (h) H_2O_2 30%, 0 ℃, 1M NaOH, 5 min; (i) HBF_4·ether (1.50 equiv.), DCM, 1 h, 0 ℃, *tert*-butyl carbamate, 30 min at 0 ℃→rt, aqueous w-up, (80%).

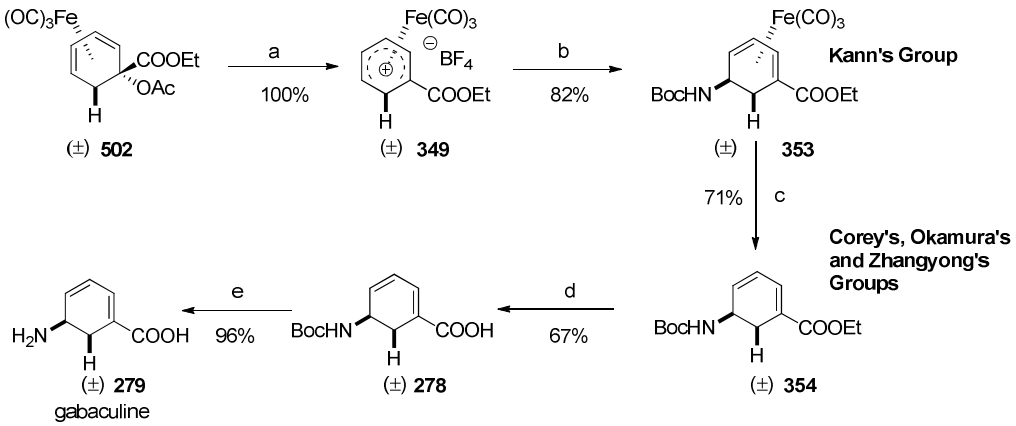
Preparation of an intermediate in Trost's synthesis **505** of oseltamivir started from microbial diol **33** delivered from benzoic acid. Acid **33** was reacted with EtI and Et_3N to afford ethyl ester in 22% yield. Ethyl ester **498** was also synthesized using CsF[243] in an improved yield of 69%. We have not optimized the conditions of this reaction. Upon treatment of **498** with diironnonacarbonyl for 5 days at *room temperature* the iron complex **499** was afforded in 61% yield which was now ready for the nucleophilic addition reaction. After 2 steps, reaction of **499**

with HBF_4−etherate, followed by treatment of cationic products with $NaBH_4$ in MeCN for 1 h, gave the expected compounds (±)-**502** and **503** in 42% and 5% yield respectively. Then the racemic mixture of (±)-**502** was treated with acid to afford salt (±)-**349** in quantitative yield, which upon treatment with potassium phthalimide and Hünig's base furnished (±)-**504** in moderate yield (73%).

Finally, (±)-**504** underwent demetallation upon treatment with an aqueous solution of H_2O_2 (30%), and 1M NaOH to provide Trost's key intermediate (±)-**505** in good yield (77%), Scheme **114**.

Our formal synthesis was not very high yielding (9.9%) due to the moderate yielding intermediate steps. Nevertheless, our route did not require any toxic and unstable azide complexes, in contrast to the originally reported route.

A further advantage of our method is that it allows the formation of (±)-**505** as a racemic mixture of a single regioisomer, rather than a regioisomeric mixture (10:1) as was reported by Trost *et al*.,[224,309] which was carried through as a mixture to the next step in their synthesis.



Scheme 115 Synthesis of Kann's key intermediate (±)-**353**, Corey's (±)-**354,** and (±)-gabaculine **279**

Reagents and conditions: (a) HBF_4·ether (1.50 equiv), DCM, −12 °C, 1 h; (b) *tert*-butyl carbamate (2.00 equiv.) DCM, 0 ℃, DIPEA (1.50 equi v.), 30 min at 0 ℃ →rt, 1 h; (c) H_2O_2 30%, 0 ℃, 1M NaOH, 5 min; (d) 2M NaOH, 2 h 50 min; (e) 4M HCl/Dioxane, 0 ℃ →rt.

With hydride (±)-**502** in hand, we envisioned that the preparation of Corey's oseltamivir intermediate would be achievable by a similar route.

The synthetic sequence for the formation of cationic iron complex (±)-**349** was optimized before. Then (±)-**349** was subjected to a nucleophilic addition with *tert*-butyl carbamate and DIPEA, and product (±)-**353** was formed and then demetallated as previously described with an aqueous solution of H_2O_2 (30%), and 1M NaOH to give (±)-**354** the key intermediate in Corey's route to oseltamivir in a very good yield of 82%, Scheme **115**.

Surprisingly, when the reaction was performed without isolation of cationic intermediate (±)-**349** and treated with *tert*-butyl carbamate, the reaction led to the novel (±)-**506** complex which was obtained after aqueous work up. The formation of (±)-**513** was circumvented by isolation of cationic (±)-**349** intermediate, before addition of any nucleophile. We did not undertake further resolution of the cationic racemic iron complex (±)-**349**.

At this point we had in hand an intermediate (±)-**354** and only 2 steps away from a natural product – gabaculine **279**. The ethyl ester (±)-**354** was hydrolysed with base and the deprotected with 4M HCl in dioxane to give final product **279** in 96% yield. Analytical data agreed with literature values.[203]

5.7 Conclusions

In this chapter we have tested various conditions of the formation of cationic η^5 intermediates, and through experimentation have found HBF_4−ether was highly efficient.

We have investigated nucleophilic addition reactions towards iron tricarbonyl cyclohexadienyl salts. We have rationalised the product distribution and designed experiments to obtain a wide range of products after nucleophilic additions and further demetallation with TMANO and/or CAN.

The enantiopurity of a derivative of a representative product of our methodology was determined using a HPLC CHIRALCEL® OD-I column and by comparison with racemic material prepared independently. At the end of this study, we prepared Trost's and Corey's tamiflu's intermediates along with gabaculine **279**.
From a synthetic view point, the results are potentially very significant, giving a chance to manipulate the outcome of the reaction by introduction of different nucleophiles.

Chapter 6

Overall summary and future work

Chapter 6: Overall summary and future work

The objective of the work presented in this thesis was the use in synthesis of microbial arene oxidation products, with the main focus on the synthesis of iron tricarbonyl cyclohexadiene ligands possessing a quaternary centre and their modification post-complexation to give a variety of useful derivatives.

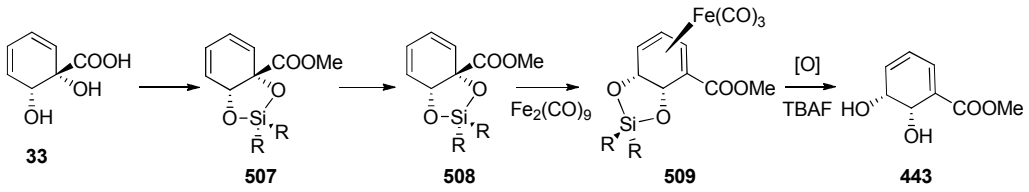
The first intermediate goal was the construction of the iron tricarbonyl complex **383** obtained directly from microbially derived diol, and its use towards the synthesis of iron cyclohexanone **396** was explored. Despite several attempts with a variety of selective oxidants, only MnO_2 led to stable irontricarbonyl ketone **396** in good yield. Parallel studies towards iron ketone derivatives were also explored. It is our opinion that further studies on the conversion of iron ketone complex **396** should be carried out, as it seems possible that formation of a cationic intermediate **422** with nucleophiles would eventually succeed.

In Chapter 4 we explored a unique rearrangement product **415**. We conducted a thorough mechanistic investigation into the formation of this compound. After additional labelling studies it appears that formation of this product is through acetonide migration rather than methyl ester group migration.

As an application of this methodology we were able to access arene 2,3-diols derivatives of non natural configuration not obtainable by bio-oxidation.

In future, we would like to explore the reactivity of the silylated cyclohexadiene ligands to prevent the formation of *endo* iron complexes. Moreover microbial diol **33** could be also protected as a derivative **507,** that will offer the advantage of being coordinated followed by spontaneous an iron tricarbonyl inducted rearrangement. This sequence, after oxidation and TBAF deprotection reaction in

neutral conditions will deliver a diol **443** of opposite stereochemistry, as depicted on Scheme **116**.



Scheme 116 Synthesis of silylated derivatives towards 2,3-diols.

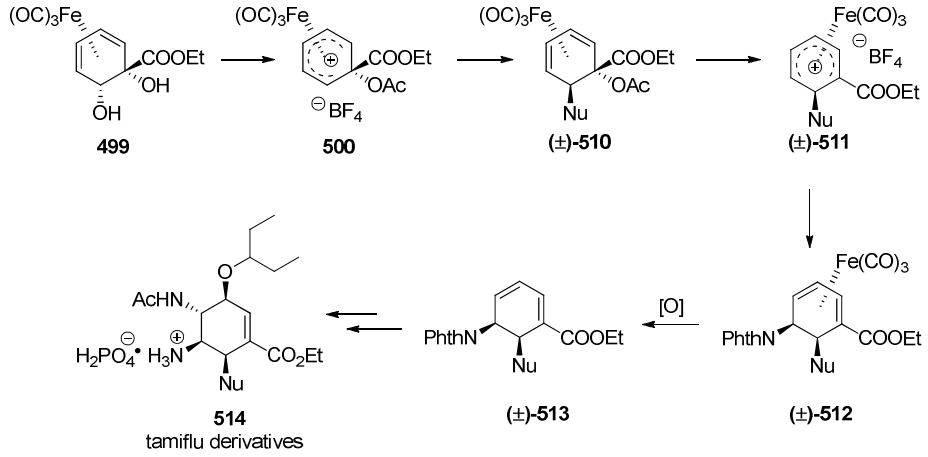
Having successfully generated rearrangement product **415** it would be significant to deliver similar iron derivative products without the acetonide protection group. Although time constraints prevented us from moving this approach forward.

In Chapter 5 the experimental conditions have been thoroughly investigated, including different solvents, as well as a variety of acids for optimisation of cationic products. The formation of these products was found to be very effective and not dependent on the amount of acid used. We have investigated nucleophilic addition reactions towards iron tricarbonyl cyclohexadienyl salts. In future, we would like to explore the introduction of a wide variety of nucleophiles to cationic intermediates and improved the yields of desired products.

The enantiopurity of a derivative of a representative product of our methodology was determined by comparison with racemic material prepared by Ogawa's protocol.

Substantial work has also been completed on an alternative synthetic route to Trost's and Corey's oseltamivir's intermediates **505** and **354** along with gabaculine **279** from *ipso*,*ortho*-diol **33**.
The above results clearly demonstrate that use of iron complexes **383** and **489** is a simple and straightforward process towards the synthesis of useful building blocks.

Our unique formal syntheses of oseltamivir will rise an opportunity to deliver wide range of derivatives as depicted in Scheme **117**. First treatment with an acid of ethyl ester complex **499** will provide a cation **500**, which is higly reactive towards series of nucleophiles. At this stage, we could create a library of novel products (±)-**510**, and after treatment with acid for a second time cationic intermediates **(±)-511** followed by potassium phthalimide will deliver products **(±)-512**, which upon oxidation will provide ligands **(±)-513**. We are interested in exploring this methodology which is a very promising tool for moderating the outcome of the reactions at any stage of nucleophilic addition. Moreover, our approach can be easily applied to the synthesis of a wide range of synthetic analogues of oseltamivir for structure-activity studies.



Scheme 117 Synthesis of novel tamiflu intermediates

Chapter 7
Experimental part

Chapter 7: EXPERIMENTAL PART

General Methods

Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. In most cases, anhydrous acetonitrile, diethyl ether, dichloromethane, hexane, toluene and tetrahydrofuran were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system.[310] All other commercially available compounds were used as obtained from the chemical suppliers. Nonacarbonyldiiron was dispensed in a glovebox.

Analytical thin layer chromatography was carried out using silver backed plates precoated with Alugram®SIL G/UV_{254nm} and plates were visualised under UV light and/or $KMnO_4$ followed by gentle warming. Organic layers were routinely dried with anhydrous $MgSO_4$ and evaporated using a Buchi rotary evaporator, and then further drying was facilitated by high vacuum. Flash column chromatography was carried out using Davisil LC 60 Å particle size silica gel (35–70 microns) purchased from Fisher Scientifics or Celite® 545 from Sigma Aldrich.

NMR spectra were run in $CDCl_3$ (unless otherwise specified) on a Brüker Avance 250, 300, 400 MHz instruments at 298K (250, 300, 400 MHz) or Brüker Avance 500 (500 MHz) instrument and recorded at the following frequencies: proton (^1H - 250/300 MHz), carbon (^{13}C - 62.9/75.4). The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet and br, broad. Chemical shifts δ are quoted in parts per million and are referenced to the residual solvent peak.

Variable temperature experiments for the kinetic studies in Chapter 4 were carried out on a Brüker AV400 spectrometer operating at 100.62 MHz for ^{13}C. Spectra were acquired in the range 232.1 – 377.4 K using a standard 13C{1H} pulse sequence, and each spectrum was acquired in the probe for at least 15 minutes at each temperature prior to data acquisition. The probe temperature was calibrated in a separate experiment by using a sample of 4% methanol in methanol-d_4.[311]

IR spectra were recorded on Perkin Elmer Spectrum 100 FTIR with diamond ATR spectrometer with only selected absorbances quoted as *v* in cm^{-1}.

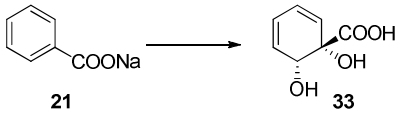
Mass spectra were recorded on a Bruker Daltonics micrOTOF mass spectrometer (Brüker Daltonik GmbH, Bremen, Germany) with electrospray time-of-flight (ESI-TOF) using either positive or negative electrospray ionisation (ESI) as stated. this was coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). The LC system was used as an autosampler only. 10µl of sample was injected into a 30:70 flow of water:acetonitrile at 0.6mL/min to the mass spectrometer. For each acquisition 10µL of calibrant of 5mM sodium formate was injected after the sample. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula.

Optical rotations were recorded on an Optical Activity, AA –10 Automatic polarimeter with a path length of 1dm. Concentrations (c) are quoted in g/100mL.

X-Ray data were collected on a Nonius KappaCCD diffractometer with Mo-Kα radiation (λ=0.71074 Á). All structures were solvent by direct methods and refined on all F^2 data using SHELX-97 suite of programmes.

All capillary melting points were recorded using a Buchi 535 melting point apparatus. The readings were taken from a mercury-in-glass thermometer and were reported uncorrected as the meniscus point. Elemental analysis was performed using an Exeter Analytical CE 440 analyzer.

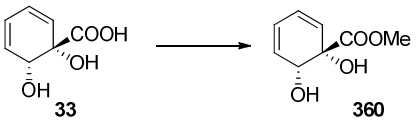
7.1 Compounds for Chapter 3



21 **33**

The conversion of benzoic acid to 1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid was effected by R. *eutrophus* B9 according to the literature procedure reported by Myers *et al*.[39] $[\alpha]_D^{25}$ −106 (*c* 0.5 in EtOH) [lit.[38], (Na^+salt) −123.8 (*c* 1.78 in H_2O); δ_H (270 MHz, $CDCl_3$ + [$^2H_6$]-DMSO); 5.4 (1H, br m, 3-H), 5.2 (1H, d m, 6-H), 5.2 (2H, br d, 4-H, 5-H), 4.1 (1H, br s, 2-H);[44]

7.1.1 Synthesis of (1*S*,2*R*)- methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate, (360)



33 **360**

Method A:

To 1.11 g (7.09 mmol, 1.00 equiv) of **33** was added benzene-MeOH (1:1, 100 mL). The resultant solution was stirred at room temperature, and (trimethylsilyl)diazomethane (2.0M solution in hexanes) was added dropwise via syringe over 15 min until effervescence ceased and a yellow colour persisted (6.5 mL). The reaction mixture was stirred for 2 h and then concentrated under reduced pressure, dried in vacuo to give the crude ester **360**, sufficiently pure to be used without further purification (1.21 g, 100%), as a white crystalline solid, mp = 51.5 – 52.5 ℃ [31], $[\alpha]_D^{20}$ − 75 ℃ ±2 (*c* 0.5 in EtOH),[44] δ_H (300 MHz, $CDCl_3$): 6.13 (1H, dd, *J* 9.5, 5.5 Hz, H-6), 5.98 (1H, ddd, *J* 3.0, 2.5, 1.0 Hz, H-5), 5.97-5.93 (1H, m, H-4), 5.83 (1H, ddd, *J* 10.0, 1.0 Hz, H-3), 5.73 (1H, dd, *J* 9.5, 1.0 Hz, C2-OH), 4.85 (1H, s, C1-OH), 3.88 (3H, s, -O-CH_3); δ_C (100 MHz, $CDCl_3$)

175.6, 132.1, 127.0, 124.8, 122.9, 74.1, 71.2, 54.0; ν_{max} (film) 3444, 3041, 1735, 1436, 1256, 1087, 1038 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_8H_{10}Na_1O_4)^+$, 193.0477; found, 193.0472.

Method B:

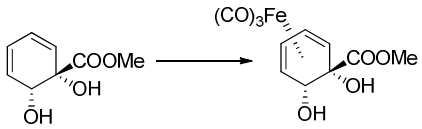
This was performed in accordance with a literature procedure.[243]

A mixture of microbial diol acid **33** (0.108 g, 0.694 mmol, 1.00 equiv), CsF (0.158 g, 1.041 mmol, 1.50 equiv) in DMF (0.8 mL) at room temperature was stirred for 2 min, followed by addition of MeI (86.4 µL, 1.388 mmol, 2.0 equiv) under nitrogen atmosphere, and stirred for 23 h at this temperature. The reaction mixture was combined with aqueous $NaHCO_3$ (15 mL), and extracted with EtOAc (3 × 20 mL). The organic layer was dried (Na_2SO_4) and evaporated. Column chromatography on silica gel (50:50 petrol-EtOAc) gave methyl ester **360** as light yellow oil (85 mg, 72%).

Method C:

This was performed in accordance with a literature procedure.[39] To a solution of (1*S*,2*R*)-1,2-dihydroxycyclohexa-3,5-diene-1-carboxylic acid **33** (6.15 g, 39.4 mmol, 1.00 equiv) in DMF (65 mL dry), NEt_3 (5.4 mL, 1.00 equiv) and MeI (2.4 mL, 1.00 equiv) were added via a syringe under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h. Then the reaction mixture was transferred to a separating funnel, diluted with EtOAc (200 mL) and extracted with sat. $LiCl_{(aq)}$ (2 × 100 mL), resulting in slow phase separation. Organic phase was dried over $MgSO_4$ and concentrated under reduced pressure without heating and purified by column chromatography [60:40 EtOAc-petroleum [(b.p. 40-60 ℃)] to give *(1S,2R)-1,2-dihydroxycyclohexa-3,5-diene-1-methyl ester* **360** as a light yellow oil; R_f 0.42 [70:30 EtOAc-petroleum [(b.p. 40-60 ℃)] (424 mg, 8%).

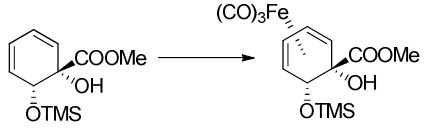
7.1.2 Synthesis of (–)-(3*S*)-Tricarbonyl(1*S*,2*S*)- methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate)iron, (383)



360 **383**

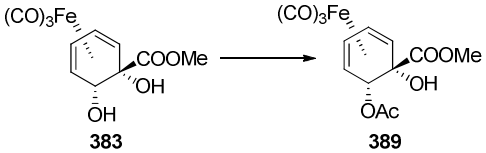
To a flask containing **360** (1.21 g, 7.08 mmol, 1.00 equiv) in a glovebox was added nonacarbonyldiiron (2.79 g, 7.67 mmol, 1.08 equiv). THF (100 mL) was added and the reaction mixture was stirred at room temperature for 7 days, then concentrated under reduced pressure (**Care! Toxic pentacarbonyliron distilled over at this point**). The crude product was purified by chromatography [40:60 EtOAc-petroleum (b.p. 40 – 60 ℃)] to give *tricarbonyl[(1S, 2R)- methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate]iron* of **383** (1.37 g, 55%). Crystals suitable for X-ray diffraction were grown from DCM/petroleum R_f 0.74 [70% EtOAc-petroleum (b.p. 40-60 ℃)]; mp 130-132 ℃; $[\alpha]_D^{25}$ −190 (c 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 5.39 (1H, dddd, *J* 6.0, 4.0, 1.5, 1.0 Hz, H-4), 5.35 (1H, ddd, *J* 6.0, 4.5, 2.0 Hz, H-5), 3.91-3.88 (1H, m, H-2), 3.88 (1H, s, C1-OH), 3.74 (3H, s, -OCH_3), 3.21 (1H, dt, *J* 6.5, 2.0 Hz, H-3), 3.17 (1H, d, *J* 7.0 Hz, C2-OH) 2.84 (1H, dd, *J* 6.0, 2.0 Hz, H-6); δ_C (75.4 MHz, $CDCl_3$) 210.2 (3 × $Fe(CO)_3$), 174.9 (-*C*$OOCH_3$), 84.6 (C-5), 84.3 (C-4), 77.3 (C-1), 72.1 (C-2), 67.4 (C-3), 64.5 (C-6), 53.5 (-COO*C*H_3); ν_{max} (film) 3417, 3007, 2957, 2202, 2176, 2049, 1958, 1723, 1436, 1381, 1236, 1172, 1135, 1062, 1020, 981, 940, 911, 869, 831, 794, 754, 732, 614 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{11}H_{10}FeO_7+Na)^+$, 332.9674; found 332.9657. (Found: C, 43.0; H, 3.22. $C_{11}H_{10}FeO_7$ requires C, 42.6; H, 3.25 %); X-ray crystal data $C_{11}H_{10}FeO_7$, M=310.04, Monoclinic, P212121, a = 8.0220(1)Å α = 90° b = 8.1780(1)Å β = 90° c = 18.1270(3)Å γ = 90°, V=1189.20(3) $Å^3$, Z=4, D_c=1.732 Mg/m^3, μ(Cu-Kα)=1.295 mm^{-1}, T=150(2) K, 25065 independent measured reflections, 2889 independent observed reflections, 193 parameters.

The crude of methyl ester **387** obtained by the Method A, was found to give silylated byproduct of (–)-(3S)-tricarbonyl(η^4-1*S*,2*S*)-methyl 1-hydroxy-2-trimethylsiloxycyclohexa-3,5-dienecarboxylate)iron(0), (**388**) at the secondary hydroxyl group, only once.



388 (1.254 g, 22%), R_f 0.27 [8:92 EtOAc-hexane] m.p. = 68 – 70 ℃, $[\alpha]_D^{25}$ –183 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.33 (2H, s, H), 4.12 (2H, d, *J* 7.0 MHz), 3.69 (3H, s, -COO*Me*), 3.06 (1H, s, H), 2.92 (1H, s, H), 0.15 (9H, s, $(CH_3)_3Si$); δ_C (75.4 MHz, $CDCl_3$) 210.4 (3 × $Fe(CO)_3$),174.3, 85.0, 84.3, 72.6, 67.0, 65.8, 52.8; ν_{max} (film) 2963, 2054, 1978, 1733, 1245, 1087, 844, 620, 605 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{18}FeO_7Na_1O_7Si)^+$, 405.0064; found 405.0146. X-ray crystal data $C_{14}H_{18}Fe\ O_7Si$, M=382.22, Monoclinic, P 2_1, a = 11.7832(2)Å $\alpha = 90^o$ b = 6.61340(10))Å $\beta = 101.4370(10)^o$ c = 22.3223(5)Å $\gamma = 90^o$, V=1704.97(5)$Å^3$, Z=4, D_c=1.489 Mg/m^3, μ(Cu-Kα)=0.985 mm^{-1}, T=150(2) K, 30516 independent measured reflections, 7382 independent observed reflections, 447 parameters.

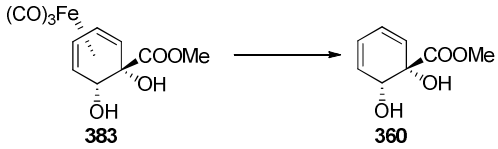
7.1.3 Synthesis of (–)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1-hydroxy-2-acetoxycyclohexa-3,5-dienecarboxylate)iron(0), (389)



To a solution of iron complex **383** (283.5 mg, 0.914 mmol, 1.00 equiv) in pyridine (20 mL) at −10 ℃, Ac_2O (10 mL) was slowly added. Stirring was continued for 18

h, at room temperature, then the reaction was quenched with H_2O (15 mL) at 0 ℃, stirred for 5 min, and extracted with EtOAc (3 × 50 mL). The organic layer was dried ($MgSO_4$), concentrated in vacuo, to afford yellow foam of **389** (293 mg, 91%), sufficiently pure to be used without further purification, R_f 0.23 [20:80 EtOAc-hexane] $[\alpha]_D^{25}$ −220 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.44 (1H, t, *J* 4.5, H-4), 5.35 (1H, t, *J* 5.0, H-5), 4.76 (1H, d, *J* 2.0, *H-2)*, 3.76 (3H, s, -COO*Me*), 3.58 (1H, s, H), 3.05 (1H, d, *J* 6.5, H-3), 2.83 (1H, d, *J* 6.0, H-6), 2.09 (3H, s, OAc); δ_C (75.4 MHz, $CDCl_3$) 209.8 (3 × $Fe(CO)_3$), 174.5, 171.5, 77.3, 84.2, 84.16, 69.9, 65.7, 61.2, 53.5, 20.5; ν_{max} (film) 3505, 2959, 2055, 1964, 1730, 1598, 1436, 1371, 1235, 1188, 1137, 1120, 1045, 979, 942, 909, 870, 793, 745, 670, 616 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{15}H_{14}FeO_9Na_1)^+$, 416.9850; found 416.9884.

7.1.4 Demetallation of (–)-(3*S*)-Tricarbonyl(1*S*,2*S*)- methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate)iron, (383)



Method A:

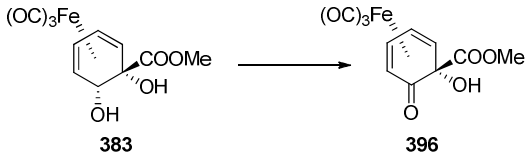
To a solution of iron complex **383** (13.5 mg, 0.043 mmol, 1.00 equiv.) in acetone (2 mL) at room temperature, solid trimethylamine *N*-oxide (22.3 mg, 6.82 equiv) was added, and left to stir for 18h at this temperature. Then the reaction mixture was filtered through a plug of Celite and washed with acetone, concentrated in vacuo, purified by column chromatography (50:50 EtOAc-Petroleum) to give 3.2 mg (43%) of deprotected diol **360** of (1*S*,2*R*)- methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate: δ_H (300 MHz, $CDCl_3$): 6.13 (1H, dd, *J* 9.5, 5.5 Hz, H-6), 5.98 (1H, ddd, *J* 3.0, 2.5, 1.0 Hz, H-5), 5.93 (1H, m, H-4), 5.83 (1H, dt, *J* 10.0, 1.0 Hz,

H-3), 5.73 (1H, dd, *J* 9.5, 1.0 Hz, C2-OH), 4.85 (1H, s, C1-OH), 3.88 (3H, s, -O-CH_3); δ_C (100 MHz, $CDCl_3$) 175.6, 132.1, 127.0, 124.8, 122.9, 74.1, 71.2, 54.0; ν_{max} (film) 3444, 3041, 1735, 1436, 1256, 1087, 1038 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_8H_{10}Na_1O_4)^+$, 193.0477; found, 193.0472.

Method B:

To a solution of iron complex **383** (54.0 mg, 0.174 mmol, 1.00 equiv.) in wet acetone (2 mL) at 0 ℃ was added a solution of ceri c ammonium nitrate (3.00 eq.) in acetone (1 mL) dropwise over 5 mins. The reaction mixture was allowed to warm to room temperature and stirred for an additional 10 min. Water was added (5 mL) and the solution was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (50:50 EtOAc-Petroleum) to give 28 mg (90%) of deprotected diol **360**.

7.1.5 Synthesis of (–)-(3*S*)-tricarbonyl(η^4-(1*S*)-methyl 1-hydroxy-2-oxocyclohexa-3,5-dienecarboxylate)iron(0), (396)



Method A: MnO_2

To **383** (983 mg, 3.17 mmol, 1.00 equiv) activated 4 Å molecular sieves (280 mg), and MnO_2 (5.51 g, 63.4 mmol, 20.00 equiv) were added. The reaction mixture was stirred at room temperature for 21 h and then filtered through a plug of Celite, washed through with CH_2Cl_2. The filtrate was concentrated under reduced pressure, concentrated in vacuo, and purified by chromatography (8:92 isopropyl alcohol-hexane) to give **396** as a yellow powder (572 mg, 59%).

Crystals suitable for X-ray diffraction were grown from CH_2Cl_2-petrol at room temperature: m.p.=122 ℃; compound R_f 0.13 [8% isopropanol-hexane); $[\alpha]_D^{25}$ −160 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 5.92 (1H, ddd, *J* 6.0, 5.0, 2.0 Hz, H-4 or H-5), 5.65 (1H, ddd, *J* 6.5, 5.0, 1.5 Hz, H4 or H-5), 4.05 (1H, s, -OH), 3.70 (3H, s, -CH_3), 3.42 (1H, dd, *J* 6.0, 1.0 Hz, H-3 or H-6), 3.34 (1H, dd, *J* 6.5, 2.0 Hz, H-6); δ_C (75.4 MHz, $CDCl_3$) 207.3 (3 × $Fe(CO)_3$), 188.8 (C2), 170.3 (-C-*C*O-O-), 86.6 (C4), 84.7 (C5), 73.1 (C1), 60.7 (C3), 56.9 (C6), 53.3 (-CH_3); ν_{max} (film) 3430, 2957, 2917, 2850, 2261, 2176, 2069 (Fe ν_{CO}), 1991(Fe vCO) , 1737 (ester vCO), 1667 (ketone vCO) , 1455, 1435, 1364, 1254, 1224, 1130, 1100, 1025, 978, 943, 871, 801, 733, 615 cm^{-1}; (ESI-TOFMS) m/z calcd for $(C_{11}H_8FeO_7 + H)^+$, 308.9697 ; found 308.9702. (Anal. Calcd for $C_{11}H_8FeO_7$: Found: C, 43.0; H, 2.60. requires C, 42.9; H, 2.62%)

X-ray crystal data $C_{11}H_8FeO_7$, M=308.02, Triclinic, P1, a = 6.6880(3)Å α = 85.896(1)° b = 6.7010(3)Å β = 85.972(2)° c = 46.634(2)Å γ = 60.254(3)°, V=1808.47(15) $Å^3$, Z=6, D_c=1.697 Mg/m^3, μ(Cu-Kα)=1.277 mm^{-1}, T=150(2) K, 14425 independent measured reflections, 8640 independent observed reflections, 1177 parameters.

Method B: py*SO_3

To a solution of **383** (80.6 mg, 0.260 mmol, 1.00 equiv) in dry DMSO (9 mL) NEt_3 (236 mg, 2.340 mmol, 9.00 eqiuv) was added dropwise and stirred for 10 minutes under nitrogen atmosphere. Separately, a solution of py·SO_3 (827 mg, 5.199 mmol, 20.00 equiv) in dry DMSO (30 mL) was prepared. This was added dropwise within 20 minutes by a cannula to the reaction mixture and left to stir for an additional 48 h. Then the reaction mixture was diluted with EtOAc (100 mL), and washed with H_2O (3 × 100 mL) and saturated aq. NaCl (3 × 100 mL) portions, 6 in total. The organic layer was dried over $MgSO_4$, and then concentrated under reduced pressure to give **396** as yellow oil (5 mg, 7%).

Method C: PCC

To a solution of iron complex **383** (17 mg, 0.055 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL) at room temperature, solid PCC (31.2 mg, 0.147 mmol, 2.66 equiv) was added, and left to stir for 23 h, under nitrogen atmosphere. Then the reaction mixture was filtered through a plug of Celite, diluted with Et_2O, and extracted with H_2O (100 mL), and 1M HCl (50 mL). Combined organic phase extracted with H_2O (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure without heating to give crude purified by column chromatography (90% Hexane-isopropanol) yielding yellow solid of **396** (10 mg, 58%).

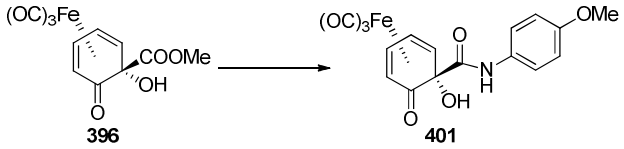
Method D: CrO_3

To a solution of **383** (20.3 mg, 0.065 mmol, 1.00 equiv) in CH_2Cl_2 (8 mL) under nitrogen atmosphere, solid CrO_3 (38.7 mg, 0.387 mmol, 6.00 equiv) and pyridine (310 µL) were added, and stirred for 2.5 hrs. The resulting black reaction mixture was filtered through a plug of Celite, diluted with Et_2O (20 mL), washed with H_2O (120 mL), 1M HCl (80 mL) and H_2O (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure without heating to give further purified by column chromatography [80:20 Hexane – isopropanol] to give **396** as a yellow solid (1.8 mg, 9%).

Method E: Ph_3CBF_4

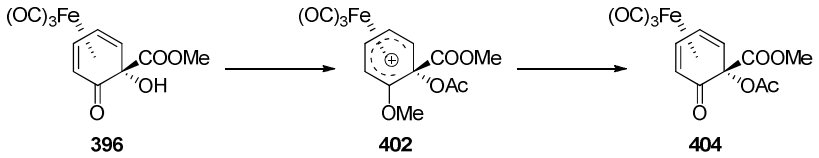
A solution of **383** (130 mg, 0.420 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL), was cooled to 0 ℃ and treated with solid triphenylcarbenium tetrafluoroborate (155 mg, 0.469 mmol, 1.11 equiv), under nitrogen atmosphere, and left to stir for 2 h. Then reaction mixture was added dropwise to Et_2O (40 mL), concentrated under reduced pressure to give crude further purified by column chromatography [60:40 EtOAc-petroleum (b.p. 40-60 ℃)] to give **396** (25 mg, 16%) as yellow oil.

7.1.6 Synthesis of *N*-4-methoxybenzyl (–)-(3*S*)-tricarbonyl(η^4-(1*S*)-methyl 1-hydroxy-2-oxocyclohexa-3,5-dienecarboxylate)iron(0) amide, (401)



To the flame dried (25 mL) flask hot MS 4 Å were added. To the flask B were added **396** (46.6 mg, 0.151 mmol, 1.00 eguiv) and catalytic amount of and *para*-toluenesulfonic acid (5 mg), under nitrogen atmosphere, Et_2O (2.5 mL) was added and transferred content into flask A via cannula. Reaction mixture was stirred at room temperature, and after 40 min, PMB-amine (20 µL, 0.158 mmol, 1.05 equiv) was added and allowed to stir for 24 h. Reaction was carried out for 9 days with extra amount of 4Å MS and $MgSO_4$, purified by column chromatography (92:8 Hexane-Isopropanol) to give **401** as a light yellow solid (5.3 mg, 8%) petroleum R_f 0.82 [20:80 Isopropanol-hexane]; $[\alpha]_D^{25}$ −75 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 7.13 (2H, d, J 8.5 Hz, MeO-C=C-*H*), 7.07 (1H, s, N*H*) 6.84 (2H, d, *J* 8.5 Hz, MeO-C=C-*H)*, 6.02 (1H, ddd, *J* 11.0, 2.0 Hz, *H*-4), 5.64 (1H, t, *J* 5.0 Hz, *H*-5), 4.27 (2H, *J* 5.5 Hz, -CH_2-NH-) 4.08 (1H, s, C1-O*H*), 3.79 (3H, s, O-CH_3) 3.54 (1H, d, *J* 5.5 Hz, =C*H*-C=O) 3.29 (1H, dd, 5.0, 2.0 Hz, =C*H*-C-OH); δ_C (75.4 MHz, $CDCl_3$) 207.6 (3 × $Fe(CO)_3$), 188.15, 169.7; 159.1; 129.5; 129.0; 114.1; 87.1; 84.8; 73.9; 61.3; 57.2; 55.3; 43.1; ν_{max} (film) 3365, 2933, 2066, 1992, 1658, 1613, 1513, 1463, 1440, 1359, 1302, 1246, 1177, 1127, 1097, 1033, 826, 733, 614 cm^{-1}; HRMS (-ve ESI-TOF) m/z calcd for $(C_{18}H_{14}FeNO_7)^-$, 412.0120; found 412.0142.

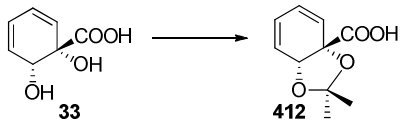
7.1.7 Synthesis of (–)-(3*S*)-tricarbonyl(η^4-(1*S*)-methyl 1-acetoxy-2-oxocyclohexa-3,5-dienecarboxylate)iron(0), (404)



To a suspension of **396** (169.4 mg, 0.549 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL) trimethyloxonium tetraflouoroborate (122.3 mg, 1.2 equiv) was added. The resulting solution was stirred at −10 ℃ for 1 h. The reaction mixture was concentrated, and dried in vacuo to give crude of **402** as yellow foam (280 mg, 100 %), used in next step without further purification. To this crude dissolved in dry MeOH (30 mL), was added a solution of sodium methoxide (48.20 mg, 1.50 equiv) in MeOH (3 mL). The reaction left to stir at -10 ℃ for 1 h, and left to stir at room temperature for 24 h. Reaction mixture was concentrated, dried in vacuo and purified by silica-gel column chromatography to afford yellow foam of **404** (159.4 mg, 83%), R_f 0.18 [20:80 EtOAc-Petrol]; $[\alpha]_D^{25}$ −10 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.87 (1H, s, H-4), 5.74 (1H, s, H-5), 3.68 (3H, s, -COO*Me*), 3.55 (1H, d, *J* 5.5 MHz, H-3), 3.44 (1H, d, *J* 4.5 MHz, H-6), 2.20 (3H, s, OAc); δ_C (75.4 MHz, $CDCl_3$) 207.3 (3 × $Fe(CO)_3$), 184.1, 170.0, 167.1, 86.3, 84.9, 77.9, 77.6, 77.1, 76.7, 62.0, 53.3, 21.0; ν_{max} (film) 2075, 2016, 1995, 1732, 1670, 1435, 1259, 1234, 1090, 610 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{10}FeO_8Na_1)^+$, 372.9620; found 372.9618.

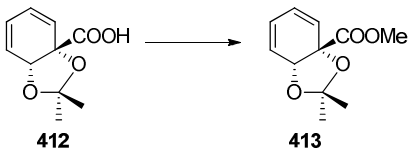
7.2 Compounds for Chapter 4

7.2.1 Synthesis of (1*S*,2*R*)-1,2-*O*-Isopropylidene-1,2-dihydroxy-cyclohexa-3,5-dienecarboxylic acid, (412)



To microbial acid **33** (1.305 g, 7.677 mmol, 1.00 equiv) and *para*-toluenesulfonic acid (0.048 g, 0.252 mmol, 0.03 equiv) in acetone (50 mL), was added 2,2-dimethoxypropane (5.947 mL, 48.365 mmol, 6.30 equiv). The reaction mixture was stirred at room temperature for 2 h, transferred to a separating funnel, washed with brnie then extracted with EtOAc (3 × 40 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concen trated under reduced pressure, purified by a silica-gel column chromatography (5:95 MeOH-CH_2Cl_2) to give colourless oil of **412** (1.452 g, 96%); δ_H (500 MHz, C DCl_3) 6.06 (2H, m) 5.92 (1H, m) 5.70 (1H, dd, *J* 9.0, 1.5 Hz) 4.85 (1H, dd, *J* 4.0, 1.0 Hz), 1.39 (3H, s, -OMe) 1.33 (3H, s, -OMe); δ_C (125 MHz, $CDCl_3$) 176.9, 124.5, 124.4, 123.9, 123.8, 107.4, 79.1, 72.8, 26.7, 25.1; ν_{max} (film) 3500, 1736, 1373, 1213, 1165, 1040 cm^{-1}; HRMS (CI) $[M+NH_4]^+$ m/z calcd for $(C_{10}H_{16}NO_4)^+$, 214.1079; found 214.1086. Data in agreement with those reported previously.[44]

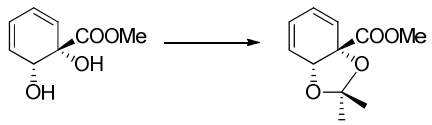
7.2.2 Synthesis of (1*S*,2*R*)-methyl 1,2-*O*-Isopropylidene-1,2-dihydroxycyclohexa-3,5-dienecarboxylate, (413)



Method A:

To a stirred solution of **412** (317 mg, 1.00 equiv) in benzene-MeOH (1:1) 100 ml, at room temperature was added dropwise (trimethylsilyl)diazomethane (2.20 mL, 2.0 M in hexanes) until the yellow colour persisted and effervescence ceased. The solution was stirred for 50 min, then concentrated under reduced pressure, dried in vacuo to give **413** a light yellow oil, sufficiently pure to be used without further purification (323 mg, 100%); δ_H (500 MHz, $CDCl_3$ 6.11 (1H, m), 6.02 (1H, m), 5.82 (1H, m), 4.97 (1H, d, *J*, 4.5 MHz), 3.79 (3H, s, -COOMe) 1.44 (3H, s, -C-CH_3), 1.42 (3H, s, -C-CH_3); δ_C (125 MHz, $CDCl_3$) 172.1, 124.7, 124.5, 124.0, 124.0, 106.7, 79.4, 72.7, 52.9, 26.8, 25.1; ν_{max} (film) 3041, 2977, 2956, 2924, 1750, 1735, 1453, 1432, 1384, 1368, 1251, 1214, 1166, 1081, 1044, 885, 805, 710 cm^{-1}; HRMS (CI) $[M+NH_4]^+$ m/z calcd for $(C_{11}H_{18}NO_4)^+$, 228.1236; found 228.1241. Data in agreement with those reported previously.[39,44]

Method B:

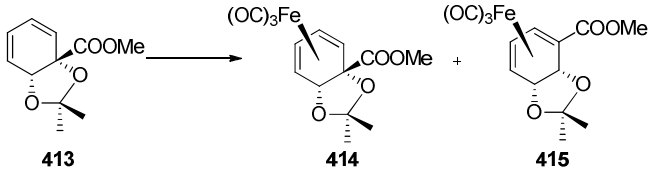


360 **413**

To methyl ester **360** (0.967 g, 5.682 mmol, 1.00 equiv) and *para*-toluenesulfonic acid (0.022 g, 0.141 mmol, 0.03 equiv) in acetone (50 mL), was added 2,2-dimethoxypropane (6.092 mL, 6.30 equiv). The reaction mixture was stirred at room temperature for 2 h, transferred to a separating funnel, washed with brnie then extracted with EtOAc (3 × 40 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concen trated under reduced pressure, dried in vacuo to give **413** a light yellow oil (1.051g, 88%) sufficiently pure to be used without further purification.

7.2.3 Synthesis of (+)-(3*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (414) and (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 2,3-isopropylidenedioxy cyclohexa-4,6-dienecarboxylate)iron, (415)

From the Crude Ester:



To a flask containing purified **413** (183 mg, 0.872 mmol, 1.00 equiv) in a glove box diiron nonacarbonyl (348 mg, 0.957 mmol, 1.09 equiv) was added. THF (100 mL) was added and the reaction mixture was stirred at room temperature for 7 days. and then concentrated under reduced pressure (**Care! Toxic pentacarbonyliron distilled over at this point**). The crude brown oil was pre-adsorbed on silica and purified by chromatography (10% EtOAc-petroleum) to give two isomers of (+)-(3*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0) of **414** (88.9 mg, 29%) as a yellow foam; crystals suitable for x-ray diffraction were grown by slow diffusion of acetone of **414;** R_f 0.58 [10:90 EtOAc-petroleum (b.p.40-60 ℃)]; $[\alpha]_D^{25}$ +60 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 5.61 (2H, dd, *J* 3.0, 7.5 Hz, H-4, H-5), 5.12 (1H, d, *J* 4.0 Hz, H-5) 3.80 (3H, s, -COO*Me*) 3.11 (1H, dd, *J* 3.0, 5.0 Hz, H-3) 3.03 (1H, dd, *J* 4.0, 7.0 Hz, *H*-6) 1.37 (3H, s, -C-CH_3) 1.15 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 171.5 (-*C*$OOCH_3$), 117.0, 87.1, 85.8, 85.7, 79.9, 57.6, 55.8, 52.8, 28.1, 27.2; ν_{max} (film) 2991, 2936, 2856, 2054, 1973, 1741, 1456, 1436, 1380, 1371, 1342, 1303, 1256, 1210, 1164, 1135, 1065, 1030, 988, 966, 937, 893, 863, 820, 792, 761, 647, 622, 613 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986; found 372.9973;

X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, C2, a = 20.7320(4)Å α = 90□ b = 6.2630(1)Å β = 110.174(1)^o c = 12.1540(3)Å γ = 90^o, V=1481.31(5) Å^3,

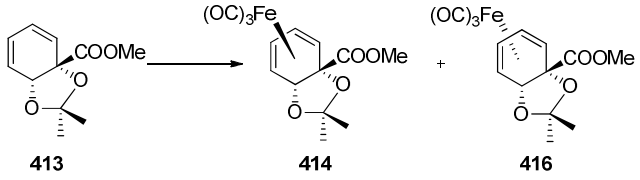
Z=4, D_c=1.570 Mg/m^3, μ(Cu-Kα)=1.050 mm^{-1}, T=150(2) K, 12804 independent measured reflections, 3232 independent observed reflections, 219 parameters.

and **415** (80.4 mg, 26%) as a yellow oil: R_f 0.48 [10% EtOAc-petroleum (b.p.40-60 ℃)]; $[\alpha]_D^{25}$ −45 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 5.41 (1H, t, *J* 4.5, 10.0 Hz, *H*-4), 5.29 (1H, t, *J* 5.0, 9.5 Hz, H-5), 4.32 (1H, d, *J* 2.0 Hz, H-2), 3.73 (3H, s, -COO*Me*) 3.34 (1H, d, *J* 5.0 Hz, H-3), 3.04 (1H, d, *J* 6.0 Hz, H-6), 1.64 (3H, s, -C-CH_3) 1.16 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$), 210.4 (3 × $Fe(CO)_3$), 174.5 (-*C*OOCH_3), 109.4, 85.7, 85.2, 83.1, 79.5, 64.3, 62.8, 53.1, 25.1, 24.4; ν_{max} (film) 2991, 2953, 2054, 1972, 1728, 1458, 1435, 1385, 1379, 1339, 1298, 1272, 1251, 1207, 1171, 1085, 1059, 1032, 1012, 973, 941, 873, 819, 801, 783, 762, 666, 644, 615 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9979; found 372.9986 (Found: C, 48.1; H, 4.11. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %);

X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, $P2_1$, a = 10.1710(4) Å α = 90□ b = 7.2170(4) Å β = 110.426(3)^o c = 10.6320(6) Å γ = 90^o, V=731.36(6) Å^3, Z=2, D_c=1.590 Mg/m^3, μ(Cu-Kα)=1.063 mm^{-1}, T=150(2) K, 7011 independent observed reflections, 203 parameters.

7.2.4 Synthesis of (+)-(3*R*)-Tricarbonyl(*η*^{4}-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (414) and (–)-(3*S*)-Tricarbonyl(*η*^{4}-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (416)

From purified ester



413 414 416

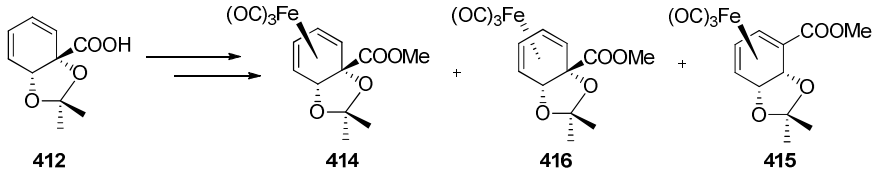
To a flask containing purified **413** (371 mg, 1.77 mmol, 1.00 equiv) in a glove box diiron nonacarbonyl (650 mg, 1.7662 mmol, 1.0 equiv) was added. THF (150 mL) was added and the reaction mixture was stirred at room temperature for 8 days, and then concentrated under reduced pressure (Care! Toxic pentacarbonyliron distilled over at this point) to give crude as a brown oily cake (344 mg), washed with DCM, pre-adsorbed on silica and purified by column chromatography [10:90 EtOAc-petroleum (b.p. 40 – 60 ℃)] to give **414** (189 mg, 29%) as a yellow oil, partially crystallize in the fridge: R_f 0.58 [10% EtOAc-petroleum (b.p.40-60 ºC)]; $[\alpha]_D^{25}$ +60 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 5.61 (2H, dd, *J* 3.0, 7.5 Hz, H-4, H-5), 5.12 (1H, d, *J* 4.0 Hz, H-5), 3.80 (3H, s, -COO*Me*), 3.11 (1H, dd, *J* 3.0, 5.0 Hz, H-3), 3.03 (1H, dd, *J* 4.0, 7.0 Hz, H-6), 1.37 (3H, s, -C-CH_3), 1.15 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 171.5 (-*C*$OOCH_3$), 117.0, 87.1, 85.8, 85.7, 79.9, 57.6, 55.8, 52.8, 28.1, 27.2; ν_{max} (film) 2991, 2936, 2856, 2054, 1973, 1741, 1456, 1436, 1380, 1371, 1342, 1303, 1256, 1210, 1164, 1135, 1065, 1030, 988, 966, 937, 893, 863, 820, 792, 761, 647, 622, 613 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986; found 372.9973; X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, C_2, a = 20.7320(4)Å α = 90° b = 6.2630(1)Å β = 110.174(1)° c = 12.1540(3)Å γ = 90°, V=1481.31(5) $Å^3$, Z=4, D_c=1.570 Mg/m^3, μ(Cu-Kα)=1.050 mm^{-1}, T=150(2) K, 12804 independent measured reflections, 3232 independent observed reflections, 219 parameters.

And **416** as a yellow oil (30.4 mg, 4%) as a yellow oil: R_f 0.48 [10:90 EtOAc-petroleum (b.p.40–60 ℃)]; $[\alpha]_D^{25}$ –45 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 5.41 (1H, t, *J* 4.5, 10.0 Hz, *H*-4), 5.29 (1H, t, *J* 5.0, 9.5 Hz, H-5), 4.32 (1H, d, *J* 2.0 Hz, H-2), 3.73 (3H, s, -COO*Me*) 3.34 (1H, d, *J* 5.0 Hz, H-3), 3.04 (1H, d, *J* 6.0 Hz, H-6), 1.64 (3H, s, -C-CH_3) 1.16 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 210.4 (3 × $Fe(CO)_3$), 174.5 (-*C*$OOCH_3$), 109.4, 85.7, 85.2, 83.1, 79.5, 64.3, 62.8, 53.1, 25.1, 24.4; ν_{max} (film) 2991, 2953, 2054, 1972, 1728, 1458, 1435, 1385, 1379, 1339, 1298, 1272, 1251, 1207, 1171, 1085, 1059, 1032, 1012, 973, 941, 873, 819, 801, 783, 762, 666, 644, 615 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for

$(C_{14}H_{14}FeO_7+Na)^+$, 372.9979; found 372.9986 (Found: C, 48.1; H, 4.11. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %);

7.2.5 Synthesis of (+)-(3*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (423) (−)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 2,3-isopropylidenedioxy cyclohexa-4,6-dienecarboxylate)iron, (424) and (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (425) in one pot.

From purified acid



To a flask containing **412** (742 mg, 3.78 mmol, 1.00 equiv) in a glovebox was added nonacarbonyldiiron (1.39 g, 3.78 mmol, 1.00 equiv). THF (350 mL) was added and the reaction mixture was stirred at room temperature for 8 days, then concentrated under reduced pressure (**Care! Toxic pentacarbonyliron distilled over at this point**) to give brown oily crude used in next step without any purification.

To this crude of acids (1.08 g, 3.23 mmol, 1.00 equiv) benzene/MeOH (1:1) was added 100 mL, flushed with nitrogen, and (trimethylsilyl)-diazomethane was added dropwise via syringe over 15 min until effervescence ceased and a yellow colour persisted (~ 6.5 mL). The reaction mixture was stirred for 2 h and then concentrated under reduced pressure, dried in vacuo to give brown oil crude esters (221 mg) further purified by column chromatography (10% EtOAc-Petroleum b.p.40–60) to give **414** (190 mg, 17%) as a yellow oil**:** R_f 0.58 [10% EtOAc-petroleum (b.p.40-60 ℃)]; $[\alpha]_D^{25}$ +60 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$)

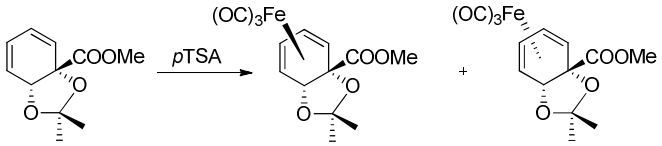
5.61 (2H, dd, *J* 3.0, 7.5 Hz, H-4, H-5), 5.12 (1H, d, *J* 4.0 Hz, H-5) 3.80 (3H, s, -COO*Me*) 3.11 (1H, dd, *J* 3.0, 5.0 Hz, H-3), 3.03 (1H, dd, *J* 4.0, 7.0 Hz, *H*-6) 1.37 (3H, s, -C-CH_3) 1.15 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 171.5 (-*C*OOCH_3), 117.0, 87.1, 85.8, 85.7, 79.9, 57.6, 55.8, 52.8, 28.1, 27.2; ν_{max} (film) 2991, 2936, 2856, 2054, 1973, 1741, 1456, 1436, 1380, 1371, 1342, 1303, 1256, 1210, 1164, 1135, 1065, 1030, 988, 966, 937, 893, 863, 820, 792, 761, 647, 622, 613 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986; found 372.9973; X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, C2, a = 20.7320(4)Å α = 90° b = 6.2630(1)Å β = 110.174(1)° c = 12.1540(3)Å γ = 90°, V=1481.31(5) $Å^3$, Z=4, D_c=1.570 Mg/m^3, μ(Cu-Kα)=1.050 mm^{-1}, T=150(2) K, 12804 independent measured reflections, 3232 independent observed reflections, 219 parameters.

And **416** (182 mg, 16%) as a yellow oil; R_f 0.48 [10:90 EtOAc-petroleum (b.p.40-60 ℃)]; $[\alpha]_D^{25}$ −45 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 5.41 (1H, t, *J* 4.5, 10.0 Hz, *H*-4), 5.29 (1H, t, *J* 5.0, 9.5 Hz, H-5), 4.32 (1H, d, *J* 2.0 Hz, H-2), 3.73 (3H, s, -COO*Me*) 3.34 (1H, d, *J* 5.0 Hz, H-3), 3.04 (1H, d, *J* 6.0 Hz, H-6), 1.64 (3H, s, -C-CH_3) 1.16 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 210.4 (3 × $Fe(CO)_3$), 174.5 (-*C*OOCH_3), 109.4, 85.7, 85.2, 83.1, 79.5, 64.3, 62.8, 53.1, 25.1, 24.4; ν_{max} (film) 2991, 2953, 2054, 1972, 1728, 1458, 1435, 1385, 1379, 1339, 1298, 1272, 1251, 1207, 1171, 1085, 1059, 1032, 1012, 973, 941, 873, 819, 801, 783, 762, 666, 644, 615 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9979; found 372.9986 (Found: C, 48.1; H, 4.11. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %);

and **415** (106 mg, 9%) as a yellow foam: R_f 0.44 [10:90 EtOAc-petroleum (b.p.40-60 ℃)]; mp 81-84 ℃; $[\alpha]_D^{25}$ +80 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 6.36 (1H, d, *J* 4.5 Hz, H-6), 5.70 (1H, t, *J* 5.0, 10.5 Hz, H-5), 5.12 (1H, d, *J* 8.5 Hz, H-2), 4.70 (1H, dd, *J* 3.5, 8.5 Hz, H-3), 3.72 (3H, s, -COO*Me*), 3.11 (1H, t, *J* 4.5, 9. Hz, H-4), 1.34 (3H, s, -C-CH_3), 1.22 (3H, s, -C-CH_3); δ_C (100.6 MHz, $CDCl_3$) 212.8, 206.6, 204,7 (3 × $Fe(CO)_3$), 171.4, 114.5, 89.8, 86.7, 75.6, 73.9, 63.3, 59.0, 55.5, 52.3, 31.4, 26.3, 24.6; ν_{max} (film) 2989, 2954, 2252, 2059, 1978,

1710, 1460, 1436, 1380, 1372, 1278, 1244, 1204, 1161, 1043, 1006, 961, 916, 891, 802, 732, 667, 641, 612 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+H)^+$, 351.0167; found 351.0164, $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986; found 372.9979. (Found: C, 47.6; H, 4.03. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %); X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, $P2_1$, a = 10.1710(4) Å α = 90° b = 7.2170(4) Å β = 110.426(3)° c = 10.6320(6) Å γ = 90°, V=731.36(6) $Å^3$, Z=2, D_c=1.590 Mg/m^3, μ(Cu-Kα)=1.063 mm^{-1}, T=150(2) K, 7011 independent observed reflections, 203 parameters.

7.2.6 Synthesis of (+)-(3*R*)-Tricarbonyl(*η*^{4}-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (414) and (−)-(3*S*)-Tricarbonyl(*η*^{4}-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), (416)



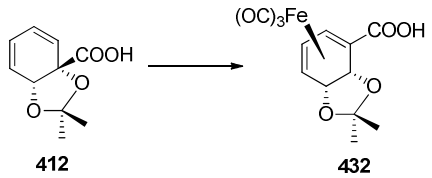
413 **414** **416**

To a flask containing purified **413** (1.309 g, 6.622 mmol, 1.00 equiv) in a glove box diiron nonacarbonyl (3.6535 g, 9.934 mmol 1.50 equiv) was added. THF (250 mL) was added and the reaction mixture was stirred at room temperature for 12 days. Into reaction mixture was added solution of *p*-toluenesulfonic acid (5 mg) via syringe in THF (3 mL). The reaction mixture was stirred at room temperature for an additional 7 days, and then concentrated under reduced pressure (Care! Toxic pentacarbonyliron distilled over at this point). The crude brown oil was pre-adsorbed on silica and purified by chromatography (10:90 EtOAc-petroleum) to give two isomers of (+)-(3*R*)-Tricarbonyl(*η*^{4}-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylate)iron(0), **414** (381 mg, 17 %) as a yellow oil; R_f 0.58 [10% EtOAc-petroleum (b.p.40-60 ℃)]; $[\alpha]_D^{25}$ +60 (*c*

0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 5.61 (2H, dd, *J* 3.0, 7.5 Hz, H-4, H-5), 5.12 (1H, d, *J* 4.0 Hz, H-5) 3.80 (3H, s, -COO*Me*) 3.11 (1H, dd, *J* 3.0, 5.0 Hz, H-3) 3.03 (1H, dd, *J* 4.0, 7.0 Hz, *H*-6) 1.37 (3H, s, -C-CH_3) 1.15 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 171.5 (-*C*$OOCH_3$), 117.0, 87.1, 85.8, 85.7, 79.9, 57.6, 55.8, 52.8, 28.1, 27.2; ν_{max} (film) 2991, 2936, 2856, 2054, 1973, 1741, 1456, 1436, 1380, 1371, 1342, 1303, 1256, 1210, 1164, 1135, 1065, 1030, 988, 966, 937, 893, 863, 820, 792, 761, 647, 622, 613 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986; found 372.9973; X-ray crystal data $C_{14}H_{14}FeO_7$, M=350.10, Monoclinic, C2, a = 20.7320(4)Å α = 90° b = 6.2630(1)Å β = 110.174(1)° c = 12.1540(3)Å γ = 90°, V=1481.31(5) $Å^3$, Z=4, D_c=1.570 Mg/m^3, μ(Cu-Kα)=1.050 mm^{-1}, T=150(2) K, 12804 independent measured reflections, 3232 independent observed reflections, 219 parameters.

And **416** (425 mg, 19%) as a yellow oil: R_f 0.48 [10:90 EtOAc-petroleum (b.p.40-60 ºC)]; $[\alpha]_D^{25}$ −45 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$), 5.41 (1H, t, *J* 4.5, 10.0 Hz, *H*-4), 5.29 (1H, t, *J* 5.0, 9.5 Hz, H-5), 4.32 (1H, d, *J* 2.0 Hz, H-2), 3.73 (3H, s, -COO*Me*) 3.34 (1H, d, *J* 5.0 Hz, H-3), 3.04 (1H, d, *J* 6.0 Hz, H-6), 1.64 (3H, s, -C-CH_3) 1.16 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 210.4 (3 × $Fe(CO)_3$), 174.5 (-*C*$OOCH_3$), 109.4, 85.7, 85.2, 83.1, 79.5, 64.3, 62.8, 53.1, 25.1, 24.4; ν_{max} (film) 2991, 2953, 2054, 1972, 1728, 1458, 1435, 1385, 1379, 1339, 1298, 1272, 1251, 1207, 1171, 1085, 1059, 1032, 1012, 973, 941, 873, 819, 801, 783, 762, 666, 644, 615 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9979; found 372.9986 (Found: C, 48.1; H, 4.11. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %);

7.2.7 Synthesis of (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*) 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylic acid)iron(0), (432)

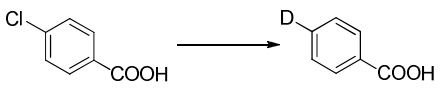


412 432

From crude acid

To a flask containing **412** (658 mg, 3.36 mmol, 1.00 equiv) in a glovebox was added nonacarbonyldiiron (1.39 g, 3.78 mmol, 1.00 equiv). THF (200 mL) was added and the reaction mixture was stirred at room temperature for 12 days, then concentrated under reduced pressure (Care! Toxic pentacarbonyliron distilled over at this point) to give brown oily further purified by column chromatography (10:90 EtOAc-Petroleum 40-60°) to give mixture of p roducts with major **432** as (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*) 1,2-isopropylidenedioxy cyclohexa-3,5-dienecarboxylic acid)iron(0); δ_H (300 MHz, $CDCl_3$) 6.36 (1H, d, *J* 1.0, 3.5 Hz, *H*-5), 5.72 (1H, dt, *J* 1.0, 5.0, 11.0, Hz, *H*-4), 5.08 (1H, dd, *J* 1.0, 8.5 Hz, H-1), 4.72 (1H, dddd, *J* 1.0, 4.0, 10.0, *H*-2), 3.16 (1H, ddt, *J* 1.0, 5.0, 10.0, *H*-3), 1.35 (3H, s, -C-CH_3), 1.23 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 176.26 (3 × $Fe(CO)_3$), 115.0, 90.2, 87.0, 76.4, 74.4, 59.2, 56.9, 26.9, 25.4; ν_{max} (film) 2989, 2916, 2850, 2061, 1980, 1682, 1552, 1463,1406, 1380, 1280, 1251, 1206, 1160, 1098, 1042, 1010, 959, 940, 895, 866, 812, 760, 732, 652, 613, 603 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{12}FeO_7+Na)^-$ 334.9854; found 334.9849;

7.2.8 Synthesis of (1*S*,2*R*)-1,2-dihydroxy-4-deuterocyclohexa-3,5-diene-1-carboxylic acid, (418)



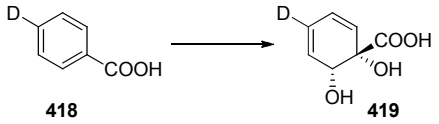
417 418

A suspension of 10% Pd/C (500 mg) in D_2O (100 mL) with **417** were placed in a 250 mL round-bottom flask, and NEt_3 were added (2.81 mL, 31.935 mmol, 1.20 equiv), and stirred under D_2 (balloon) at room temperature for 48 h. The reaction

mixture was diluted with Et_2O, filtered, and neutralised using 5% $NaHSO_4$ aqueous solution and extracted with Et_2O (3 × 50 mL). Combined organic phase was washed successively with water (50 mL) and brnie (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give colourless solid **418** (3.01 g, 77%).

The D content was determined by ^1H NMR of the corresponding methyl ester on the basis of the integration of the methyl protons. Data for methyl ester of [D]-**418**: δ_H (400 MHz, CD_3OD): 3.93 (s, 3H), 7.49 (d, *J* 5.9 Hz, 2 H), 7.62 (m, 0.060 H), 8.04 ppm (d, *J* 5.9 Hz, 2H);[275]

7.2.9 (1*S*,2*R*)-4-deutero-1,2-dihydroxycyclohexa-4,6-dienecarboxylic acid, (419)

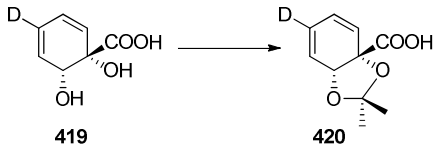


418 **419**

The conversion of deuterated benzoic acid to (1*S*,2*R*)-4-deutero-1,2-dihydroxycyclohexa-4,6-dienecarboxylic acid, (**419**) was effected by R. *eutrophus* B9 according to the literature procedure reported by Myers et al.[39]

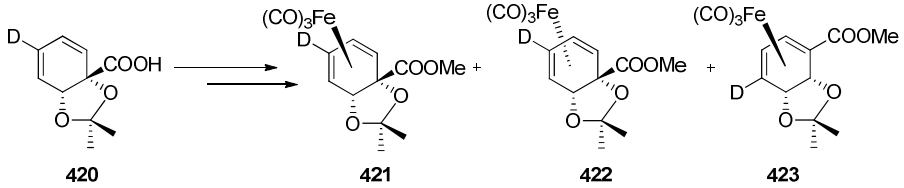
Isolated **419** as a cream powder (744 mg, 19%) $[\alpha]_D^{25}$ −90 (*c* 0.1, CH_3OH); δ_H (300 MHz, CD_3OD); 6.10 (1H, d, *J* 7.5, H-5), 5.80-5.78 (2H, m, H-3, H-6), 4.85 (1H, br s, H-2*)*; δ_C (75.4 MHz, CD_3OD) 177.9, 133.4, 127.2, 127.0, 123.6 (t, $^1J_{CD}$ 33.0 Hz),75.4, 72.3; ν_{max} (film) 3281, 3060, 2879, 2432, 2229, 2072, 1695, 1576, 1397, 1357, 1330, 1309, 1267, 1221, 1171, 1150, 1078, 1050, 1008, 976, 912, 877, 861, 803, 766, 750, 656 cm^{-1}; HRMS (-ve ESI-TOF) m/z calcd for $(C_7H_7DO_4–H)^-$, 156.0490; found 156.0412.

7.2.10 Synthesis of (1*S*,2*R*)-1,2-*O*-Isopropylidene-1, 2dihydroxy-4-deuterocyclohexa-3,5-dienecarboxylic acid, (420)



To (1*S*,2*R*)-4-deutero-1,2-dihydroxycyclohexa-4,6-dienecarboxylic acid **419** (255mg, 1.622 mmol, 1.00 equiv) and and *para*-toluenesulphonic acid (8.5 mg, 0.04 mmol, 0.03 equiv) in acetone (20 mL), was added 2,2-dimethoxypropane (0.833 mL, 9.440 mmol, 6.30 equiv). The reaction mixture was stirred at room temperature for 2 h, transferred to a separating funnel, washed with brnie then extracted with EtOAc (3 × 40 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give colourless oil of **420** (241 mg, 75%); $[\alpha]_D^{25}$ −310 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$) 6.13 (1H, d, *J* 9.5, H-5), 5.99 (1H, d, *J* 3.5 H-3), 5.81 (1H, d, *J* 9.5, H-6) 4.95 (1H, d, *J* 4.0, H-2), 1.46 (3H, s, -C-CH_3) 1.41 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 176.8, 124.6, 124.5, 124.2, 124.0, 123.9, 123.5, 107.6, 79.4, 77.6, 77.2, 76.7, 73.0, 31.0, 26.9, 25.3; v_{max} (film) 2991, 2939, 2256, 1717, 1457, 1376, 1246, 1211, 1165, 1094, 1042, 966, 909, 867, 822, 780, 728, 667, 647, 631 cm^{-1}; HRMS (-ve ESI-TOF) m/z calcd for $(C_{10}H_{10}D_1O_4)^-$, 196.0720; found 196.0694.

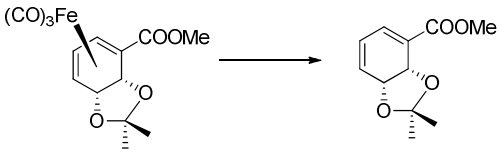
7.2.11 Synthesis of (+)-(3*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy-4-deuterocyclohexa -3,5-dienecarboxylate)iron(0), (421) (−)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 2,3-isopropylidenedioxy-4-deuterocyclohexa -4,6-dienecarboxylate)iron(0), (422) and (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy5-deuterocyclohexa -3,5-dienecarboxylate)iron(0), (423)



To a flask containing acidic acetonide **420** (240 mg, 1.230 mmol, 1.00 equiv) in a glovebox was added nonacarbonyldiiron (799 mg, 2.172 mmol, 2.17 equiv). THF (100 mL) was added and the reaction mixture was stirred at room temperature for 9 days, then concentrated under reduced pressure (Care! Toxic pentacarbonyliron distilled over at this point). The crude brown oil was used in next step without further purification. To a stirred solution of this crude (410 mg, 1.00 equiv) in benzene-MeOH (1:1) 100 ml, at room temperature was added dropwise (trimethylsilyl)diazomethane (8 mL, 2.0 M in hexanes) until the yellow colour persisted and effervescence ceased. The solution was stirred for 50 min solvent, then concentrated under reduced pressure, dried in vacuo and pre-adsorbed on silica and purified by silica-gel column chromatography (10% EtOAc-petroleum) to give **three** isomers of (+)-(3*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy-4-deuterocyclohexa -3,5-dienecarboxylate)iron(0), **421** (116.5 mg, 29%) as a yellow foam; R_f 0.30 [10% EtOAc- hexane]; $[\alpha]_D^{25}$ +40 (c 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.63 (1H, dd, *J* 1.0, 6.0, H-5), 5.13 (1H, d, *J* 4.0, H-2), 3.82 (3H, s, -COO*Me*), 3.12 (1H, d, *J* 6.5, H-6), 3.04 (1H, d, *J* 1.0, 4.0, H-3) 1.38 (3H, s, -C-CH_3), 1.16 (3H, s, -C-CH_3); δ_C

(75.4 MHz, $CDCl_3$) 210.1 (3 × $Fe(CO)_3$), 174.1, 109.0, 84.8, 82.6, 80.1, 64.0, 62.3, 52.8, 24.8, 24.0; ν_{max} (film) 2993, 2955, 2053, 1966, 1739, 1457, 1438, 1380, 1370, 1303, 1255, 1208, 1164, 1060, 1026, 984, 919, 891, 867, 817, 792, 761 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{13}DFeO_7Na_1)^+$, 374.0050; found 374.0047; and (−)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 2,3-isopropylidenedioxy-4-deuterocyclohexa -4,6-dienecarboxylate)iron(0), **422** (37 mg, 10%) as a yellow oil; R_f 0.20 [10% EtOAc- hexane]; $[\alpha]_D^{25}$ −90 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.30 (1H, dd, *J* 1.0, 6.5, H-5), 4.43 (1H, d, *J* 3.0, H-2), 3.73 (3H, s, -COO*Me*), 3.35 (1H, dd, *J* 1.0, 2.5, H-6), 3.05 (1H, d, J 6.5, H-3), 1.65 (3H, s, -C-CH_3), 1.57 (3H, s, -C-CH_3); ν_{max} (film) 2924, 2852, 2054, 1969, 1729, 1459, 1436, 1378, 1326, 1298, 1249, 1206, 1170, 1115, 1085, 1060, 1031, 973, 939, 891, 851, 820, 802, 784, 758, 665, 613 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{13}DFeO_7Na_1)^+$, 374.0050; found 374.0055; and (−)-(4*R*)-Tricarbonyl(η^4-(1*S*,2*S*)-methyl 1,2-isopropylidenedioxy5-deuterocyclohexa -3,5-dienecarboxylate)iron(0), **423** (10.7 mg, 1.8%) as a yellow foam; R_f 0.16 [10% EtOAc- hexane]; $[\alpha]_D^{25}$ −70 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 6.36 (1H, d, *J* 4.0 Hz), 5.71 (1H, d, *J* 4.5 Hz), 5.13 (1H, d, *J* 9.0 Hz*)*, 4.71 (1H, d, *J* 8.5 Hz, H), 3.73 (3H, s, -COO*Me*), 1.35 (3H, s, -C-C*H*$_3$), 1.23 (3H, s, -C-CH_3); δ_C (75.4 MHz, $CDCl_3$) 171.4, 115.0, 89.9, 86.9, 74.7, 60.4, 52.1, 27.1, 25.6; ν_{max} (film) 2988, 2936, 2060, 1982, 1713, 1458, 1437, 1373, 1338, 1318, 1298, 1262, 1244, 1205, 1160, 1095, 1064, 1012, 961, 905, 878, 814, 661, 632, 612 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{13}DFeO_7Na_1)^+$, 374.0050; found 374.0056.

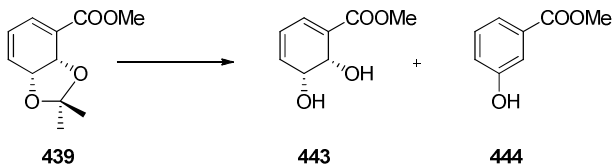
7.2.12 Synthesis of (–)-(2*S*,3*R*)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate, (439)



415 **439**

To **415** (123 mg, 0.350 mmol, 1.0 equiv) and trimethylamine-*N*-oxide (1.05 g, 14.0 mmol, 39.9 equiv) under N_2 was added benzene (50 mL). The reaction mixture was stirred at rt for 5 h. Diethyl ether (50 mL) was then added and precipitate was thoroughly dislodged from the flask walls with a spatula. The reaction mixture was transferred to a separating funnel and extracted with H_2O (2 × 70 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and dried under high vacuum to give (–)-(2*S*,3*R*)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate **439** (54 mg, 73%) as a light brown oil; R_f 0.48 (20% EtOAc-hexane); $[\alpha]_D^{25}$ −108 (*c* 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.14 (1H, d, *J* 5.0 Hz, H-6), 6.12 (1H, dd, *J* 10.0, 2.5 Hz, H-4), 6.09 (1H, dd, *J* 10.0, 5.0 Hz, H-5), 4.93 (1H, d, *J* 8.5 Hz, H-2), 4.87 (1H, dd, *J* 8.5, 2.5 Hz, H-3), 3.82 (3H, s, -OCH_3), 1.46 (3H, s, -CCH_3), 1.39 (3H, s, -CCH_3); data in agreement with those reported previously[312]; δ_C (75.5 MHz, $CDCl_3$, 298 K) 166.7 (-COOCH3), 134.0 (C-4), 133.9 (C-6), 126.1 (C-1), 121.3 (C-5), 105.6 (H3C-C-CH3), 72.5 (C-3), 68.1 (C-2), 52.1 (-OCH3), 26.7 (-CCH_3), 25.1 (-CCH_3); ν_{max} (film) 2988, 2921, 1715, 1589, 1437, 1371, 1297, 1259, 1161, 1108, 1082, 1030, 864, 707 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{11}H_{14}O_4+Na)^+$, 233.0790, found 233.0779.

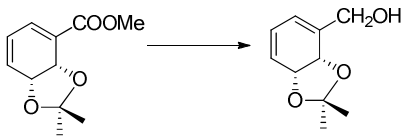
7.2.13 Formation of (2*S*,3*R*)-methyl 2,3-dihydroxycyclohexa-4,6-dienecarboxylate 443 observed by NMR.



439 **443** **444**

Isopropylidene **439** (22.0 mg, 0.105 mmol, 1.0 equiv) was dissolved in CD_3OD (1mL) in a Young's NMR tube. Iodine (15.4 mg, 0.0607 mmol, 0.58 equiv.) was added. The NMR sample was heated to 50 ℃ and ^{1}H-NMR spectra were acquired a five minute intervals. Formation of the diol **443** was observed, but subsequently it was converted to an aromatic byproduct **444**.

7.2.14 Synthesis of (–)-(2S,3R)-(2,3-isopropylidenedioxycyclohexa-4,6-dienyl)methanol, (440)

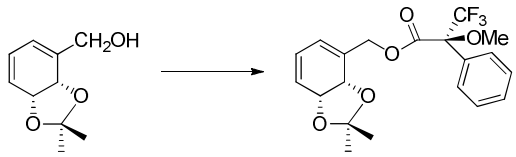


439 440

Ester **439** (50 mg, 0.238 mmol, 1.0 equiv) was dissolved in diethyl ether (10 mL) under nitrogen atmosphere at −78 ℃. Separately, li thium aluminium hydride (9.0 mg, 0.238 mmol, 1.0 equiv) was dissolved in diethyl ether (3.0 mL) and added dropwise via cannula to the reaction mixture. The reaction mixture was stirred for 15 min, and warm up to room temperature. The reaction mixture was then stirred at this temperature for additional 0.5 h, and then a saturated aqueous solution of Rochelle's salt (30 mL) was added dropwise. The biphasic mixture was stirred vigorously at room temperature for 1 h, then an additional portion of diethyl ether (10 mL) was added and the mixture was transferred to a separating funnel. The layers were separated and the aqueous layer was extracted with additional portions of diethyl ether (4 × 40 mL). Combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by chromatography (30% EtOAc-hexane) to give (–)-(2*S*,3*R*)-(2,3-isopropylidenedioxycyclohexa-4,6-dienyl)methanol **440** (12.5 mg, 29%) as a colourless oil; R_f 0.21 (30% EtOAc-hexane); $[\alpha]_D^{25}$ −75 (*c* 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 6.03 (1H, dd, *J* 9.5, 5.5 Hz, H-5), 5.97 (1H, dq, *J* 5.5, 1.0 Hz,

H-6), 5.89 (1H, ddd, *J* 9.5, 1.5, 1.0 Hz, H-4), 4.73 (1H, d, *J* 7.5 Hz, H-2 or H-3), 4.70 (1H, d, *J* 9.5 Hz, H-2 or H-3), 4.32 (1H, d, *J* 14.0 Hz, -CHHOH), 4.29 (1H, d, *J* 14.0 Hz, -CH*H*OH), 2.11 (1H, br s, -OH), 1.41 (3H, s, -C-CH_3), 1.41 (3H, s, -C-CH_3); δ_C (75.5 MHz, $CDCl_3$, 298 K) 136.1 (C-1), 124.6 (C-4), 124.0 (C-5), 119.5 (C-6), 105.5 (H_3C-C-CH_3), 71.8 (C-2), 71.0 (C-3), 64.6 (-CH_2OH), 26.8 (-CCH_3), 24.8 (-CCH_3); ν_{max} (film) 3575, 3416, 3044, 2985, 2930, 1734, 1611, 1541, 1406, 1371, 1304, 1246, 1207, 1158, 1033, 950, 877, 820, 791, 756, 718, 694 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{14}O_3+Na)^+$, 205.0841, found 205.0834.

7.2.15 Synthesis of (–)-(2'*S*,*3'R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate, (442)

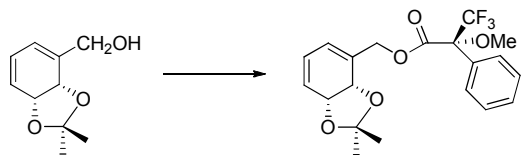


440 **442**

Alcohol **440** (21.2 mg, 0.116 mmol, 1.0 equiv) and (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate[280] (54.5 mg, 0.233 mmol, 2.00 equiv, 95% *e.e.*) were dissolved in CH_2Cl_2 (0.5 mL) at room temperature. *N*,*N*-Dimethylaminopyridine (2.5 mg, 0.020 mmol, 0.09 equiv) in CH_2Cl_2 (0.3 mL) was added by syringe, followed by *N*,*N*'-diisopropylcarbodiimide (29.4 mg, 0.233 mmol, 2.00 equiv). The reaction mixture was stirred at room temperature for 17 h, then concentrated under reduced pressure. A ^{1}H–NMR spectrum of the crude was acquired, then purification by chromatography (30% EtOAc-hexane) gave **442** (–)-(2'*S*,3'*R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate (40 mg, 87%) as a white gum; R_f 0.68 (30% EtOAc-hexane); $[\alpha]_D^{25}$ –30 (c 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.53-7.52 (2H, m, Ar-H), 7.41-7.34 (3H, m, Ar-H), 6.01-5.97 (2H, m, H'-5, H'-6), 5.94-5.91 (1H,

m, H'-4), 5.05 (1H, d, *J* 13.0 Hz, -CHH-O-), 4.89 (1H, d, *J* 13.0 Hz, -CHH-O-), 4.65 (1H, dd, *J* 9.0, 3.5 Hz, H'-3), 4.52 (1H, d, *J* 9.0 Hz, H'-2), 3.56 (3H, s, $-OCH_3$), 1.37 (6H, s, 2× C-CH_3); δ_C (125.8 MHz, $CDCl_3$, 298 K) 166.3 (C=O), 132.2, 130.8, 130.1, 129.6, 128.7, 127.4, 126.9, 125.9, 123.3, 123.3 (q, $^1J_{CF}$ 287 Hz, $-CF_3$), 122.7, 105.6 (H_3C-C-CH_3), 84.7 (q, $^2J_{CF}$ 27 Hz, CCF_3), 70.7, 70.5, 66.6 ($-CH_2O-$), 55.5 ($-OCH_3$), 26.7 ($-CCH_3$), 24.7 ($-CCH_3$); δ_F (376.5 MHz, $CDCl_3$, 298 K) -71.5; ν_{max} (film) 2968, 1754, 1452, 1372, 1171, 1122, 1017, 719, 642 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{20}H_{21}F_3O_5+Na)^+$, 421.1239, found 421.1238.

7.2.16 Synthesis of (+)-(2'*S*,3'*R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate, (441)



440 **441**

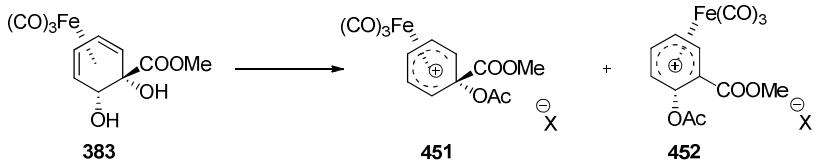
Alcohol **440** (20.1 mg, 0.111 mmol, 1.0 equiv) and (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate[280] (60.0 mg, 0.256 mmol, 2.31 equiv, 99% e.e.) were dissolved in CH_2Cl_2 (1.2 mL) at room temperature. *N*,*N*-Dimethylaminopyridine (2.0 mg, 0.016 mmol, 0.15 equiv) in CH_2Cl_2 (0.3 mL) was added by syringe, followed by *N,N*'-diisopropylcarbodiimide (28.0 mg, 0.222 mmol, 2.00 equiv). The reaction mixture was stirred at rt for 17 h, then concentrated under reduced pressure. A ^{1}H NMR spetrum of the crude was acquired , then purification by chromatography (20% EtOAc-hexane) gave **441** (–)-(2'*S*,3'*R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate (32 mg, 72%) as a white gum; R_f 0.58 (20% EtOAc-hexane);

$[\alpha]_D^{25}$ +10 (c 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.57-7.52 (2H, m, Ar-H), 7.44-7.36 (3H, m, Ar-H), 6.02-5.99 (2H, m, H'-5, H'-6), 5.95-5.92 (1H, m, H'-4), 4.99 (1H, d, *J* 13.0 Hz, -CHH-O-), 4.94 (1H, d, *J* 13.0 Hz, -CHH-O-), 4.62 (1H, dd, *J* 9.0, 3.5 Hz, H'-3), 4.51 (1H, d, *J* 9.0 Hz, H'-2), 3.58 (3H, s, $-OCH_3$), 1.37 (3H, s, $C-CH_3$), 1.36 (3H, s, $C-CH_3$); δ_C (100.6 MHz, $CDCl_3$, 298 K) 166.3 (C=O), 132.3, 130.7, 129.7, 129.6, 128.8, 127.3, 126.8, 125.8 (q, $^1J_{CF}$ 276 Hz, $-CF_3$), 125.8, 123.4, 122.9, 105.6 ($H_3C-C-CH_3$), 84.7 (q, $^2J_{CF}$ 27 Hz, $-CCF_3$), 70.6, 70.4, 66.7 ($-CH_2O-$), 55.6 ($-OCH_3$), 26.7 ($-CCH_3$), 24.7 ($-CCH_3$); δ_F (376.5 MHz, $CDCl_3$, 298 K) -71.5; ν_{max} (film) 2988, 1749, 1672, 1498, 1452, 1372, 1236, 1168, 1122, 1018, 766, 710, 655 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{20}H_{21}F_3O_5+Na)^+$, 421.1239, found 421.1240.

7.3 Compounds for Chapter 5

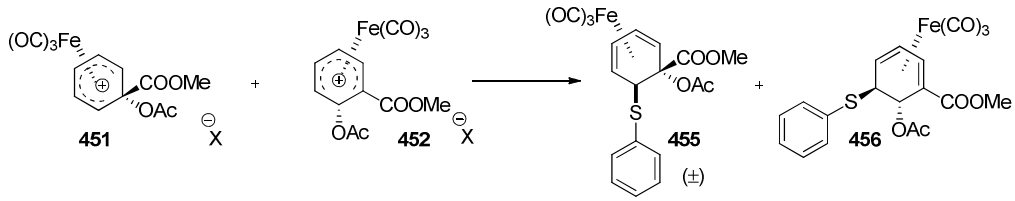
General Experimental Procedures

1. **General procedure (A) for formation of cationic η^5-dienyl complexes (451 and 452) with acid* in acetic anhydride.**



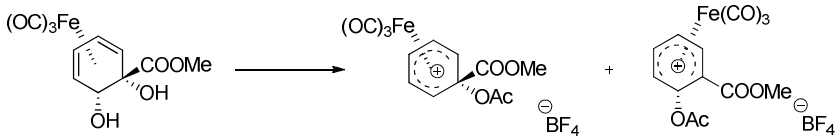
Acid* (TFA, HOTf, HPF_6, HBF_4, $HBF_4{\cdot}OEt_2$) (~ 10.00 eq.) was added to a stirred solution of the neutral complex **383** (~ 0.10 g, 0.322 mmol, 1.00 eq.) in acetic anhydride (3.2 mL) at −12 °C, under nitrogen atmosphere, and stirred at this temperature for 1 h. To the reaction mixture, cold dried Et_2O was added (60 mL) dropwise and light yellow precipitate was formed and filtered by suction, washed with cold Et_2O (3 × 5 mL). After concentration and recrystalisation of resultant acidic solution with ^{t}BuOMe, an additional amount of products were afforded to give mixture of products **451** and **452**. The crude cation mixture was used immediately in the next step.

2. **General procedure (B) for NaSPh addition reactions.**



The procedure (**A**) for the formation of cationic products was undertaken and to a resultant solution of the cationic products in dry THF, MeCN or Ac_2O (0.20 M) at 0 ℃ was added solid sodium thiophenolate (1.374 mm ol, 4.28 eq.). The mixture was stirred for 1hr at this temperature, under nitrogen atmosphere. The resultant yellow suspension was quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (SiO_2, 10% hexanes-ethyl acetate) to afford two products **455** and **456** (1,2- and 2,3-additions).

3. General procedure (C) for formation of cationic η^5-dienyl complexes with HBF_4 in diethyl ether in acetic anhydride.



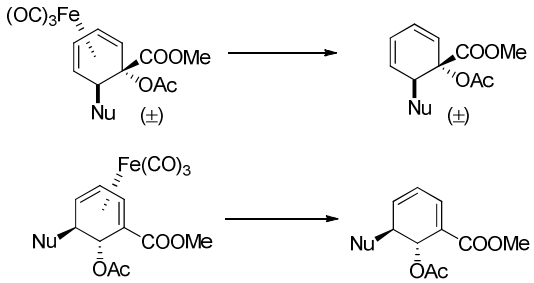
Tetrafluoroboric acid in diethyl ether (10.00 eq.) was added dropwise to a stirred solution of the neutral complex **383** (~0.20 g, 0.645 mmol, 1.00 eq.) in acetic anhydride (~ 6.2 mL, 0.1 M) at −12 ℃ for 1 h, unde r nitrogen atmosphere. The reaction mixture was transferred to cold Et_2O (150 mL) and light yellow precipitate was formed and filtered by suction, washed with cold Et_2O (3 × 10mL). Recrystalization with ^{t}BuOMe afforded two products **451**&**452**, in 83% overall yield. The crude cation mixture was used immediately in the next step.

4. General procedure (D) for nucleophilic addition reactions of (–)-Tricarbonyl(η^5-(2*S*)-methyl 2-acetoxycyclohexadienylcarboxylate)iron(I) tetrafluoroborate and (–)-

(1S)-Tricarbonyl(η^5-(1S)-methyl 1-acetoxycyclohexadienylcarboxylate)iron(I) tetrafluoroborate.

The procedure (C) for the formation of cationic products was undertaken and to a resultant solution of the cationic products in dry THF or CH_3CN (5 mL) at 0 ℃ was added a nucleophile (5.00 eq.). The reaction mixture was stirred at this temperature, under nitrogen atmosphere for 1 h, and then quenched by addition of H_2O. The product extracted with EtOAc or Et_2O (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by column chromatography (SiO_2, hexanes-ethyl acetate) to afford the products.

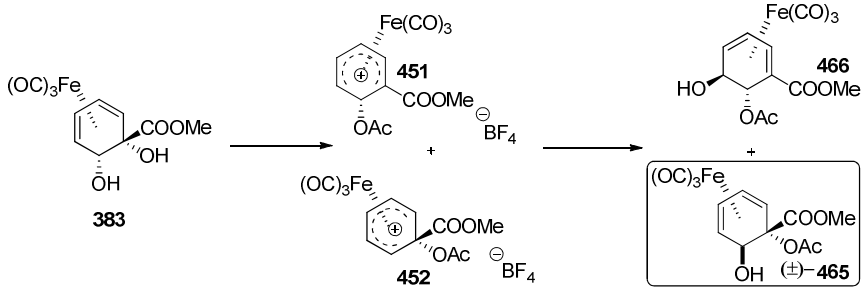
5. General procedure for the demetallation of diene iron complexes



Method A: To a solution of anhydrous trimethylamine *N*-oxide (TMANO) (36.00 eq.) in dry benzene (5 mL) was added a solution of iron complex in benzene (50 mL), and then the solution was stirred at room temperature, under nitrogen atmosphere for 24 h. To the brown resultant solution was added water (80 mL) and extracted with diethyl ether (2 × 20 mL). The organic layer was dried ($MgSO_4$) and evaporated to give crude further purified by silica-gel column chromatography.

Method B: To a solution of the relevant iron complex in wet acetone (2 mL) at 0 ℃ was added a solution of ceric ammonium nitrate (3.00 eq.) in acetone (1 mL) dropwise over 5 mins. The reaction mixture was allowed to warm to room temperature and stirred for an additional time period (specified). Water was added (5 mL) and the solution was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography.

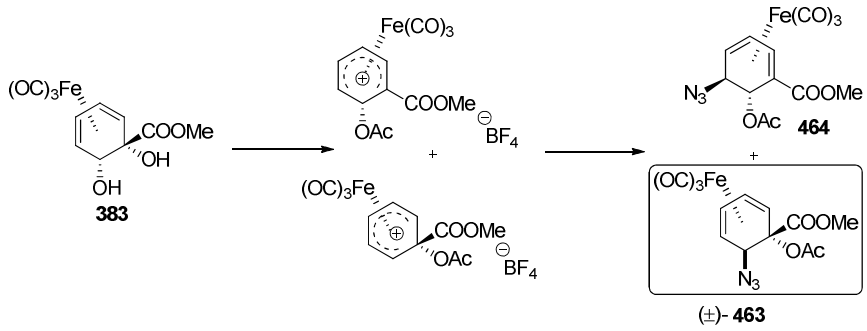
7.3.1 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*R*)-methyl 1-acetoxy-2-hydroxycyclohexa-3,5-dienecarboxylate)iron(0), (465)



Formation of (±)-465. In accordance with the general procedure, employing MeCN at 0 ℃ to r.t. with 233 mg of **383** and with a 0.1M aqueous solution of NaOH as nucleophile, gave **465** as a light yellow foam (64.8 mg, 25%) R_f 0.36 [40:60 EtOAc-Petrol]; δ_H (400 MHz, $CDCl_3$); 5.61 (1H, ddd, *J* 6.0, 4.0, 1.5 Hz, H-5), 5.47 (1H, t, *J* 5.5 Hz, H-4), 4.17 (1H, dd, *J* 7.0, 3.5 Hz, H-2), 3.70 (3H, s, -$COOCH_3$), 3.20 (1H, d, *J* 6.5 Hz, H-6), 3.13 (1H, ddd, *J* 5.0, 3.5, 1.5 Hz, H-3), 2.71 (1H, d, *J* 7.0 Hz, -OH), 2.15 (3H, s, -$OC(O)CH_3$); δ_C (100.6 MHz, $CDCl_3$) 209.9 (3 × $Fe(CO)_3$), 170.6, 169.8, 85.2, 85.1, 84.0, 77.6, 61.1, 55.7, 53.0, 21.2; ν_{max} (film) 3421, 2956, 2923, 2853, 2157, 2050, 1966, 1739, 1714, 1432, 1367, 1333, 1270, 1236, 1205, 1136, 1101, 1069, 1049, 1025, 992, 964, 929, 909, 872, 814, 763, 734, 705, 674 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for

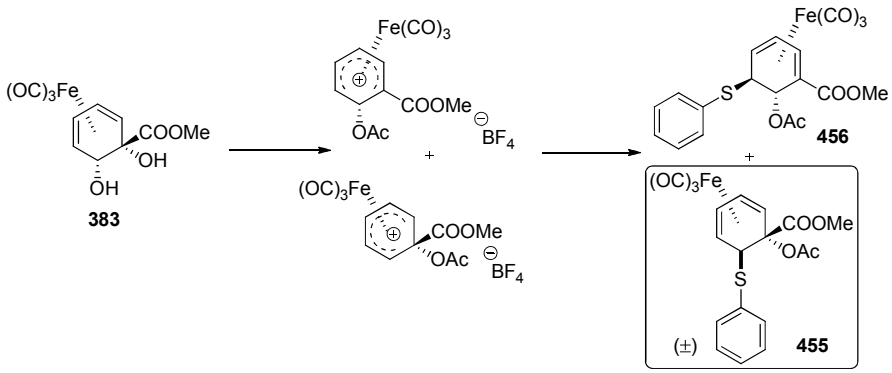
$(C_{13}H_{12}O_8FeNa_1)^+$, 374.9782; found 374.9779. Elemental analysis: C, 44.7; H, 3.56. $C_{13}H_{12}FeO_8$ requires C, 44.35; H, 3.44%.

7.3.2 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*R*)-methyl 1-acetoxy-2-azidecyclohexa-3,5-dienecarboxylate)iron(0), (463)



Formation of (±)-463. In accordance with the general procedure, employing THF at 0 ℃ to r.t. with 195 mg of **383**, gave **463** as yellow foam, 81.4 mg (34%) R_f 0.56 [20:80 EtOAc-Hexane]; mp: 124-126 ℃; δ_H (250 MHz, $CDCl_3$); 5.69 (1H, t, *J* 4.5 Hz, H-5), 5.59 (1H, t, *J* 5.0 Hz, H-4), 3.90 (1H, d, *J* 3.5 Hz, H-2), 3.72 (3H, s, -$COOCH_3$), 3.54 (1H, d, *J* 6.0 Hz, H-6) 3.05 (1H, t, *J* 4.5 Hz, H-3), 2.15 (1H, s, -$OC(O)CH_3$); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 170.0, 168.1, 86.9, 85.1, 84.2, 68.0, 57.1, 55.2, 53.0, 21.3; ν_{max} (film) 2956, 2237, 2100, 2054, 1971, 1740, 1450, 1435, 1369, 1331, 1222, 1138, 1063, 1041, 1012, 993, 946, 915, 869, 812, 766, 733, 716, 672, 649 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{11}FeN_3O_7Na_1)^+$, 399.9844; found 399.9829. Elemental analysis: C, 41.5; H, 2.97; N, 10.7. $C_{13}H_{11}FeN_3O_7$ requires C, 44.41; H, 2.94; N, 11.14%.

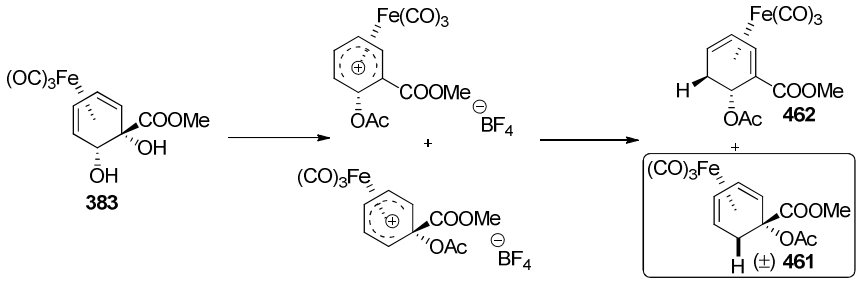
7.3.3 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*R*)-methyl 1-acetoxy-2-tiophenylcyclohexa-3,5-dienecarboxylate)iron(0), (455)



Formation of 455. In accordance with the general procedure, employing THF at –78 ℃ to r.t., with 82 mg of **383** gave **455** as a beige solid (52.4 mg, 45%) R_f 0.28 [10:90 EtOAc-Hexane]; mp: 117-118 ℃; δ_H (250 MHz, $CDCl_3$); 7.39-7.35 (2H, m, *o*-Ar-*H*), 7.33-7.27 (3H, m, *p*+*m*-Ar-*H*), 5.64 (1H, ddd, *J* 6.0, 4.0, 1.5 Hz, H-5), 5.39 (1H, td, *J* 5.5, 1.0 Hz, H-4), 3.77 (1H, d, *J* 6.5 Hz, H-6), 3.66 (3H, s, -COO*C*H_3), 3.64 (1H, d, *J* 4.0 Hz, H-2), 3.29 (1H, ddt, *J* 5.0, 3.5, 1.5, H-3), 2.18 (3H, s, -OC(O)CH_3); δ_C (75.4 MHz, $CDCl_3$) 210.0 (3 × Fe(CO)3), 170.2, 168.9, 136.2, 131.0, 129.1, 127.2, 87.3, 86.6, 83.9, 61.1, 58.9, 57.6, 52.7, 21.5; ν_{max} (film) 3067, 2951, 2332, 2258, 2152, 2052, 1967, 1739, 1582, 1481, 1438, 1367, 1276, 1243, 1219, 1138, 1086, 1061, 1049, 1025, 987, 948, 909, 866, 809, 732, 691 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{19}H_{16}FeO_7S_1Na_1)^+$, 466.9863; found 466.9850. Elemental analysis: C, 52.1; H, 3.73. $C_{19}H_{16}FeO_7S$ requires C, 51.37; H, 3.63%;

X-ray crystal data $C_{19}H_{16}FeO_7S$, M=444.23, Triclinic, P1, a = 7.3200(1)Å α = 97.505(1)□ b = 10.5210(2)Å β = 103.386(1)^o c = 13.3490(2)Å γ = 102.216(1)^o, V=959.88(3) $Å^3$, Z=2, D_c=1.537 Mg/m^3, μ(Cu-Kα)=0.933 mm^{-1}, T=150(2) K, 18914 independent measured reflections, 3921 independent observed reflections, 272 parameters.

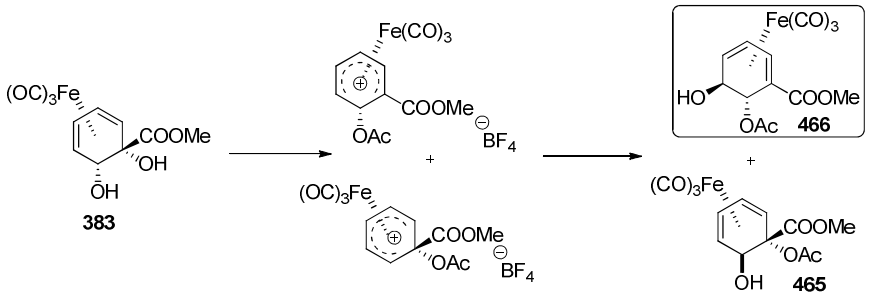
7.3.4 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*)-methyl 1-acetoxycyclohexa-3,5-dienecarboxylate)iron(0), (461)



Formation of (±)-461. In accordance with the general procedure, employing MeCN at 0 ℃ to r.t. with 200 mg of **383**, gave **(±)-461** as a yellow foam 68.8 mg (31%) R_f 0.45 [20:80 EtOAc-Hexane]; mp: 89-91 ℃, δ_H (300 MHz, $CDCl_3$); 5.46 (1H, t, *J* 5.5 Hz, H-4), 5.35 (1H, ddd, *J* 6.0, 4.0, 1.0 Hz, H-5), 3.65 (3H, s, -$COOCH_3$), 3.16 (1H, dd, *J* 4.0, 2.0 Hz, H-3), 3.05 (1H, d, *J* 6.5 Hz, H-6), 2.71 (1H, dd, *J* 16.0, 1.0 Hz, H-2), 2.07 (3H, s, -O(C(O)CH_3), 1.91 (1H, dd, *J* 16.5, 3.5 Hz, H-2); δ_C (75.4 MHz, $CDCl_3$) 210.5 (3 × $Fe(CO)_3$), 171.8, 170.1, 87.1, 82.3, 81.4, 61.5, 60.4, 52.9, 39.9, 21.0; ν_{max} (film) 2957, 2048, 1961, 1735, 1436, 1371, 1330, 1273, 1248, 1200, 1125, 1056, 1014, 969, 947, 899, 865, 843, 810, 762, 674, 612, 624 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{12}FeO_7Na_1)^+$, 358.9830; found 358.9825. Elemental analysis: C, 47.1; H, 3.92. $C_{13}H_{12}FeO_7$ requires C, 46.46; H, 3.60%;

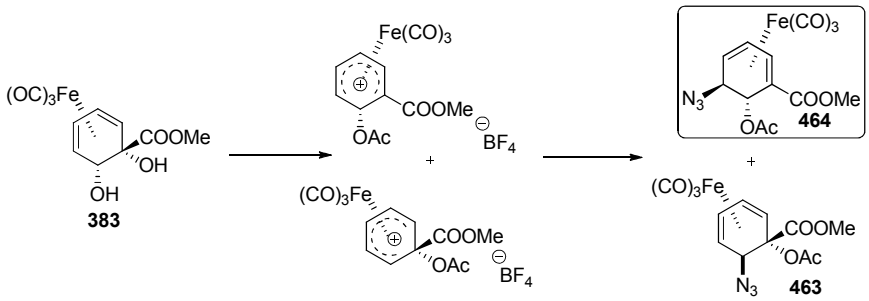
X-ray crystal data $C_{13}H_{12}FeO_7$, M=336.08, Monoclinic, $P2_1/n$, a = 9.9550(2)Å α = 90° b = 5.9360(1) Å β = 91.773(1)° c = 22.9660(5)Å γ = 90°, V=1356.48(5) $Å^3$, Z=4, D_c=1.646 Mg/m^3, μ(Cu-Kα)=1.143 mm^{-1}, T=150(2) K, 23752 independent measured reflections, 2590 independent observed reflections, 209 parameters.

7.3.5 Synthesis of (–)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-methyl 2-acetoxy-3-hydroxycyclohexa-4,6-dienecarboxylate)iron(0), (466)



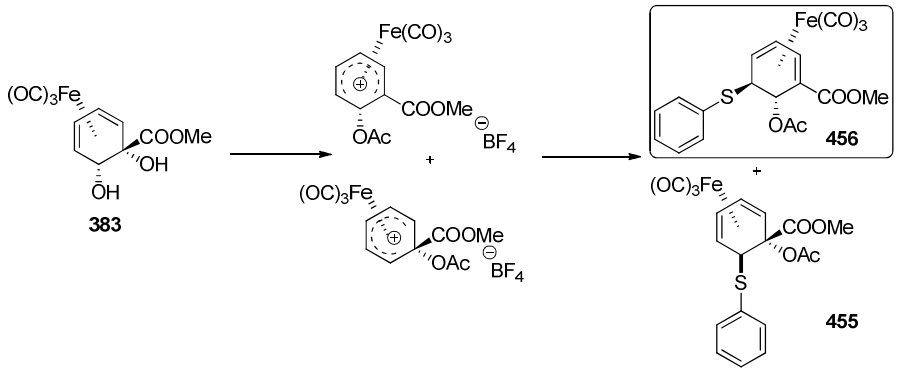
Formation of 466. In accordance with the general procedure, employing MeCN at 0 ℃ to r.t. with 233 mg of **383** and with a 0.1M aqueous solution of NaOH as nucleophile, gave **466** as a yellow oil, 27.6 mg (10%), R_f 0.26 [40% EtOAc-Petrol]; $[\alpha]_D^{25}$ +190 (*c* 0.1, CH_2Cl_2); δ_H (250 MHz, $CDCl_3$); 6.07 (1H, dd, *J* 4.5, 1.0 Hz, H-6), 5.61 (1H, t, *J* 5.5 Hz, H-5), 4.66 (1H, s, H-2), 3.87 (1H, br, H-3), 3.68 (3H, s, -$COOCH_3$), 3.12 (1H, t, *J* 5.5 Hz, H-4), 2.70 (1H, d, *J* 3.0 Hz, -OH), 2.12 (3H, s, -$O(C(O)CH_3$); δ_C (75.4 MHz, $CDCl_3$) 171.4, 171.4, 91.3, 83.9, 76.9, 76.6, 61.7, 59.2, 52.1, 21.1; ν_{max} (film) 3412, 2059, 1984, 1750, 1713, 1436, 1374, 1271, 1237, 1100, 1034, 969, 919, 873, 775, 685 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{12}O_8FeNa_1)^+$, 374.9782; found 374.9774. Elemental analysis: C, 43.9; H, 3.64. $C_{13}H_{12}FeO_8$ requires C, 44.35; H, 3.44%.

7.3.6 Synthesis of (–)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-methyl 2-acetoxy-3-azide cyclohexa-4,6-dienecarboxylate)iron(0), (464)



Formation of 464. In accordance with the general procedure, employing THF at 0 ℃ to r.t. with 195 mg of **383**, gave **464** as light yellow oil (12.4 mg, 5%) R_f 0.43 [20:80 EtOAc-Hexane]; $[\alpha]_D^{25}$ +430 (*c* 0.1, CH_2Cl_2); δ_H (250 MHz, $CDCl_3$); 6.09 (1H, dd, *J* 4.5, 1.0 Hz, H-6), 5.67 (1H, t, *J* 5.0 Hz, H-5), 4.95 (1H, s, H-2), 3.68 (3H, s, -$COOCH_3$), 3.58 (1H, d, *J* 4.5 Hz, H-3), 3.14 (1H, td, *J* 5.5, 1.0 Hz, H-4), 2.11 (3H, s, -$OC(O)CH_3$); δ_C (75.4 MHz, $CDCl_3$) 208.4 (3 × $Fe(CO)_3$), 170.9, 169.4, 91.7, 82.9, 73.0, 66.9, 63.6, 55.8, 52.2, 21.0; ν_{max} (film) 2955, 2096, 2059, 1982, 1746, 1713, 1456, 1435, 1369, 1323, 1275, 1225, 1151, 1099, 1032, 971, 926, 872, 814, 775, 745, 611 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{11}FeN_3O_7\ Na_1)^+$, 399.9844; found 399.9846. Elemental analysis: C, 41.6; H, 3.00; N, 10.7. $C_{13}H_{11}FeN_3O_7$ requires C, 44.41; H, 2.94; N, 11.14%.

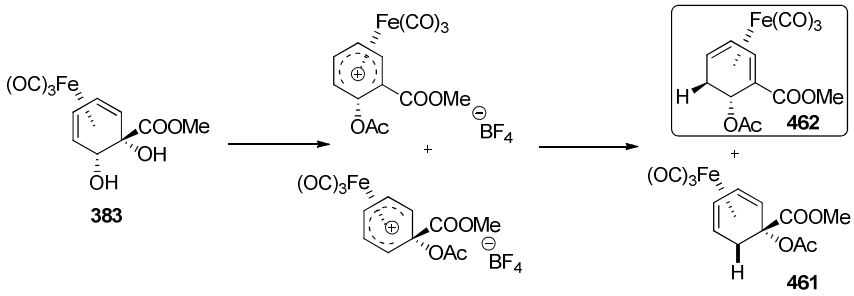
7.3.7 Synthesis of (–)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-methyl 2-acetoxy-3-tiophenylcyclohexa-4,6-dienecarboxylate)iron(0), (456)



Formation of 456. In accordance with the general procedure, employing THF at –78 ℃ to rt, with 82 mg of **383** gave **456** as a yellow oil, 7.3 mg (6%). R_f 0.15 [10:90 EtOAc-Hexane]; $[\alpha]_D^{25}$ +20 (*c* 0.05, CH_2Cl_2); δ_H (250 MHz, $CDCl_3$); 7.44-7.42 (2H, m, *o*-Ar-H), 7.32-7.29 (3H, m, *para*+*meta*-Ar-H), 5.91 (1H, d, *J* 4.0 Hz, H-6), 5.41 (1H, t, *J* 5.0 Hz, H-5), 5.24 (1H, s, H-2), 3.65 (3H, s, -$COOCH_3$), 3.30 (1H, s, H-4), 3.26 (1H, br, H-3), 2.05 (3H, s, -$OC(O)CH_3$); δ_C (75.4 MHz, $CDCl_3$) 208.9 (3 × $Fe(CO)_3$), 171.0, 169.3, 134.3, 129.7, 129.0, 128.4, 90.1, 83.0, 72.8,

64.8, 60.8, 55.2, 52.0, 21.0; ν_{max} (film) 2340, 2203, 2146, 2061, 1991, 1749, 1717, 1438, 1370, 1272, 1229, 1097, 1026, 143, 693 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{19}H_{16}FeO_7S_1Na_1)^+$, 466.9864; found 466.9861. Elemental analysis: C, 51.3; H, 3.64; $C_{19}H_{16}FeO_7S_1$ requires C, 51.37; H, 3.63.

7.3.8 Synthesis of (–)-(4*S*)-Tricarbonyl(η^4-(2*S*)-1-methyl 2-acetoxycyclohexa-4,6-dienecarboxylate)iron(0), (462)



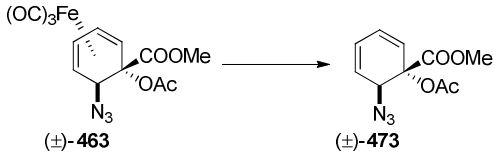
Formation of 462. In accordance with the general procedure, employing MeCN at 0 ℃ to r.t. with 200 mg of **383**, gave **462** as a yellow foam, 9.5 mg (4%). R_f 0.30 [20:80 EtOAc-Hexane]; $[\alpha]_D^{25}$ +280 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$); 5.94 (1H, d, *J* 3.0 Hz, H-6), 5.52 (1H, t, *J* 5.0 Hz, H-5), 5.03 (1H, d, *J* 6.5 Hz, H-2), 3.68 (3H, s, -$COOCH_3$), 3.20 (1H, br s, H-4), 2.09 (1H, dd, *J* 16.0, 6.5 Hz, H-3), 2.07 (3H, s, -$OC(O)CH_3$), 1.58 (1H, dd, *J* 16.0, 3.5 Hz, H-3); δ_C (75.4 MHz, $CDCl_3$) 209.4 (3 × $Fe(CO)_3$), 171.7, 170.2, 90.3, 84.5, 77.4, 68.1, 58.7, 51.9, 34.3, 21.2; ν_{max} (film) 2952, 2850, 2055, 1972, 1737, 1713, 1583, 1435, 1368, 1343, 1270, 1235, 1132, 1097, 1042, 1029, 991, 969, 894, 865, 802, 775, 715, 685 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{13}H_{12}FeO_7Na_1)^+$, 358.9830; found 358.9834. Elemental analysis: C, 46.6; H, 3.71. $C_{13}H_{12}FeO_7$ requires C, 46.46; H, 3.60%.

7.3.9 Synthesis of (±)-(1*S*,2*R*)-methyl 1-acetoxy-2-hydroxycyclohexa-3,5-dienecarboxylate, (474)

CAN Method

Formation of (±)-474. Reaction of 13.8 mg of (±)-**465** for 25 min gave a beige solid, 8.8 mg (100%). R_f 0.48 [50:50 EtOAc:Petrol]; δ_H (400 MHz, $CDCl_3$); 6.33 (1H, d, *J* 9.5 Hz, H-6), 6.17 (1H, dd, *J* 9.5, 5.0 Hz, H-5), 6.09 (1H, dd, *J* 9.5, 5.0 Hz, H-4), 6.01 (1H, dd, *J* 9.5, 5.0 Hz, H-3), 4.36 (1H, dd, *J* 8.5, 4.5 Hz, H-2), 3.80 (3H, s, -$COOCH_3$), 2.05 (3H, s, -$OC(O)CH_3$), 1.94 (1H, d, *J* 9.0 Hz, -OH); δ_C (100.6 MHz, $CDCl_3$) 170.0, 169.9, 126.6, 126.5, 124.4, 124.3, 79.6, 68.6, 52.9, 20.9; ν_{max} (film) 3452, 2955, 2056, 1985, 1732, 1436, 1412, 1370, 1273, 1232, 1136, 1078, 1047, 1019, 1000, 953, 920, 879, 812, 729, 796 694, 620 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{12}O_5Na_1)^+$, 235.0577; found 235.0616; for $(C_{20}H_{24}O_{10}Na_1)^+$, 447.1262; found 447.1255.

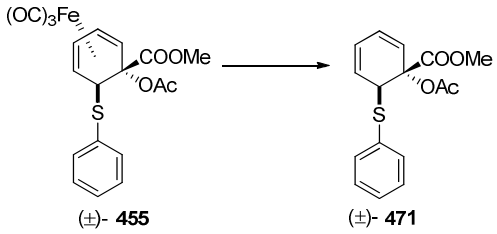
7.3.10 Synthesis of (±)-(1*S*,2*R*)-methyl 1-acetoxy-2-azidecyclohexa-3,5-dienecarboxylate, (473)



Formation of (±)-473. Reaction of 77.3 mg of (±)-**463** for 4 h gave a white solid, 34.9 mg (64%). R_f 0.27 [10:90 EtOAc-hexane]; δ_H (300 MHz, $CDCl_3$); 6.49 (1H, d *J* 9.5 Hz, H-6), 6.37 (1H, dd *J* 9.5, 5.5 Hz, H-4), 6.20 (1H, dd *J* 9.5, 5.5 Hz, H-5), 5.90 (1H, dd *J* 9.0, 5.0 Hz, H-3), 3.86-3.83 (1H, m, H-2), 3.83 (3H, s, -$COOCH_3$), 2.02 (3H, s, -$OC(O)CH_3$); δ_C (75.4 MHz, $CDCl_3$) 169.6, 169.4, 126.8, 126.6,

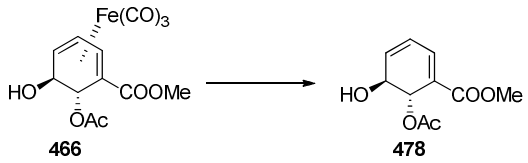
124.7, 120.1, 77.3, 57.7, 53.3, 20.7; ν_{max} (film) 2957, 2101, 1744, 1438, 1371, 1272, 1235, 1075, 1021, 937, 852, 808, 746 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{11}N_3O_4Na_1)^+$, 260.0642; found 260.0625.

7.3.11 Synthesis of (±)-(1*S*,2*R*)-methyl 1-acetoxy-2-tiophenylcyclohexa-3,5-dienecarboxylate, (471)



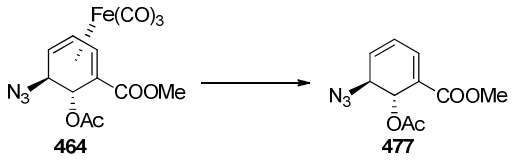
Formation of (±)-471. Reaction of 63.8 mg of (±)-**455** for 5 min gave a brown oil 37.1 mg, (85%) R_f 0.42 [20:80 EtOAc-Hexane]; δ_H (500 MHz, $CDCl_3$): 7.49-7.47 (2H, m Ar-H), 7.28-7.25 (3H, m, Ar-H), 6.36 (1H, d, *J* 9.5 Hz, H-6), 5.99-5.91 (3H, m, H-3,4,5), 4.04 (1H, d, *J* 4.5 Hz, H-2), 3.65 (3H, s, -$COOCH_3$), 1.99 (3H, s, -$OC(O)CH_3$); δ_C (125.8 MHz, $CDCl_3$): 169.6, 169.5, 134.8, 131.3, 128.3, 127.0, 125.1, 123.2, 122.9, 79.6, 52.4, 48.6, 20.7; ν_{max} (film) 2951, 2058, 1995, 1742, 1581, 1473, 1438, 1368, 1268, 1229, 1131, 1074, 1012, 986, 951, 909, 752, 717, 691, 651, 631 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{16}H_{16}S_1O_4Na_1)^+$, 327.0667; found 327.0687.

7.3.12 Synthesis of Methyl *trans*-5-hydroxy-6-acetoxy-1,3-cyclohexadiene-1-carboxylate, (478)



Formation of 478. Reaction of 14.7 mg of **466** for 5 min gave a white solid, 4.7 mg (53%). R_f 0.19 [35:65 EtOAc:hexane]; $[\alpha]_D^{25}$ +400 (*c* 0.1, CH_2Cl_2); δ_H (500 MHz, $CDCl_3$); 7.26-7.25 (1H, m, H-6), 6.29-6.28 (2H, m, H-4,5), 5.89 (1H, d, *J* 2.5 Hz, *H-2*), 4.34 (1H, s, H-3), 3.78 (3H, s, -COOMe), 2.34 (1H, d, *J* 6.0 Hz, O*H*), 2.07 (3H, s, OAc); δ_C (125.8 MHz, $CDCl_3$) 171.0, 166.2, 135.2, 133.0, 125.2, 124.2, 70.7, 67.7, 52.2, 21.2; ν_{max} (film) 3444, 2955, 2922, 2853, 2008, 1741, 1714, 1651, 1587, 1438, 1407, 1371, 1230, 1121, 1082, 1020,992, 960, 917, 876, 815, 743, 682 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{12}O_5Na_1)^+$, 235.0577; found 235.0616; for $(C_{20}H_{24}O_{10}Na_1)^+$, 447.1262; found 447.1278.

7.3.13 Synthesis of Methyl *trans*-5-azydo-6-acetoxy-1,3-cyclohexadiene-1-carboxylate, (477)

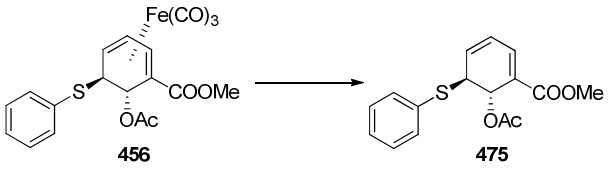


CAN Method

Formation of 477. Reaction of 26.4 mg of **464** for 3 h gave a colourless oil, 10.5 mg (63%). R_f 0.27 [20:80 EtOAc-Hexane]; $[\alpha]_D^{25}$ +840 (*c* 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$); 7.30 (1H, dd, *J* 6.0, 0.5 Hz, H-6), 6.52 (1H, dd, *J* 9.5, 6.0 Hz, H-5), 6.21 (1H, dd, *J* 9.5, 5.5 Hz, H-4), 5.93 (1H, dd, *J* 2.0, 1.0 Hz, H-2), 4.00 (1H, dd, *J* 5.5, 1.5 Hz, H-3), 3.80 (3H, s, -$COOCH_3$), 2.04 (3H, s, -$OC(O)CH_3$); δ_C (125.8 MHz, $CDCl_3$) 170.0, 165.7, 135.4, 127.6, 126.5, 125.4, 66.1, 56.4, 52.3, 21.1; ν_{max} (film) 2917, 2850, 2097, 1744, 1718, 1438, 1371, 1289, 1259, 1226, 1082,

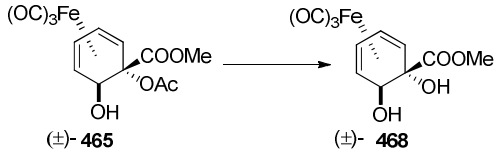
1022, 757 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{11}O_4N_3Na_1)^+$, 260.0642; found 260.0621.

7.3.14 Synthesis of Methyl *trans*-5-tiophenyl-6-acetoxy-1,3-cyclohexadiene-1-carboxylate, (475)



Formation of 475. Reaction of 3.4 mg of **456** for 5 min gave a white solid, 2.1 mg (91%) R_f 0.35 [20:80 EtOAc-Hexane]; $[\alpha]_D^{25}$ +40 (*c* 0.1, CH_2Cl_2); δ_H (500 MHz, $CDCl_3$); 7.53-7.50 (2H, m, Ar-H), 7.31-7.30 (3H, m, Ar-H), 7.13 (1H, d, *J* 5.5 Hz, H-6), 6.28 (1H, dd, *J* 9.0, 5.5 Hz, H-4), 6.24 (1H, dd, *J* 9.0, 5.5 Hz, H-5), 6.08 (1H, s, H-3), 4.08 (1H, d, *J* 5.5 Hz, H-2), 3.77 (3H, s, -COOMe), 1.98 (3H, s, $-OC(O)CH_3$); δ_C (125.8 MHz, $CDCl_3$) 170.3, 166.2, 135.7, 133.9, 132.2, 129.0, 128.5, 123.8, 123.7, 67.7, 52.2, 46.4, 29.8, 21.2; ν_{max} (film) 2924, 2854, 2064, 2064, 2004, 1743, 1715, 1580, 1439, 1369, 1286, 1228, 1078, 1025, 991, 951, 749, 694 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{16}H_{16}S_1O_4Na_1)^+$, 327.0667; found 327.0663.

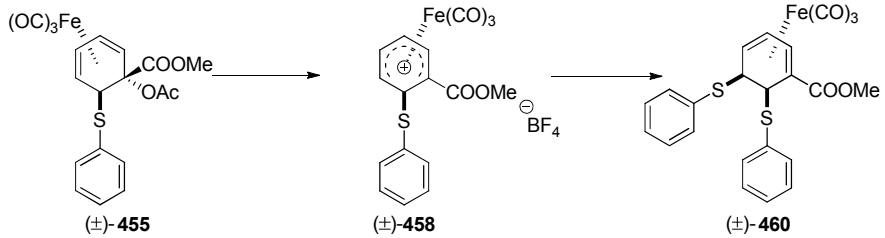
7.3.15 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*R*)-methyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate)iron(0), (468)



Methanolysis of (±)-465 to give (±)-468. To a solution of **465** (64.8 mg, 0.184 mmol, 1.00 equiv) in MeOH (dry, 8 mL) under nitrogen atmosphere, was added solid sodium methoxide (118 mg, 3.68 mmol, 20.0 eq.), and stirred for 24 h at room temperature. The resulting reaction mixture was diluted with EtOAc (15 mL), then washed with H_2O (15 mL). The organic phase dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford (±)-**468** as a yellow powder (20 mg, 35%). R_f 0.35 [50:50 EtOAc-Petrol]; δ_H (300 MHz, $CDCl_3$); 5.55 (1H, t, *J* 4.5 Hz), 5.40 (1H, t, *J* 4.5 Hz), 4.07 (1H, br s), 3.77 (3H, s, -$COOCH_3$), 3.71 (1H, s), 3.07 (1H, br s), 2.74 (1H, d, *J* 6.0 Hz); δ_C (75.4 MHz, $CDCl_3$) 210.0 (3 × $Fe(CO)_3$), 173.7, 84.8, 84.5, 81.5, 62.0, 59.1, 53.5; ν_{max} (film) 3426, 3361, 2059, 1983, 1708, 1274, 1122, 1014 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{11}H_{10}O_7FeNa_1)^+$, 332.9673; found 332.9673.

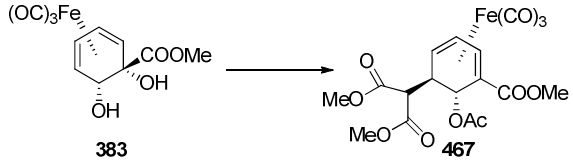
X-ray crystal data $C_{11}H_{10}FeO_7$, M=310.04, Triclinic, P1, a = 6.9380(2))Å α = 99.162(3)^o b = 7.4496(3)Å β 99.099(3)^o c = 12.0918(4)Å γ = 95.993(3)^o, V=603.82(4) $Å^3$, Z=2, D_c=1.705 Mg/m^3, μ(Cu-Kα)=1.275 mm^{-1}, T=150(2) K, 2129 independent measured reflections, 1672 independent observed reflections, 193 parameters.

7.3.16 Synthesis of (±)-(4*S*)-Tricarbonyl(*η*^{4}-(2*R*,3*R*)-1-methyl 2,3-ditiophenylcyclohexa-4,6-dienecarboxylate)iron(0), (460)



Formation of 460. In accordance with the general procedure, employing THF at –78 ℃ to r.t., with 82 mg of **455** gave **460** as a yellow oil, 10.8 mg (8%). R_f 0.24 [10:90 EtOAc-hexane]; δ_H (300 MHz, $CDCl_3$); 7.56 (2H, d, *J* 7.0 Hz, 2x*meta*-H-Ar-1), 7.42 (2H, d, *J* 7.0 Hz, 2x*meta*-H-Ar-2), 7.35-7.25 (6H, m, *ortho,para*-H-Ar-1,2), 6.11 (1H, d, *J* 4.0 Hz), 5.43 (1H, t, *J* 10.5, 5.0 Hz), 4.34 (1H, d, *J* 10.0 Hz), 4.22 (1H, dd, *J* 9.5, 2.0 Hz), 3.68 (3H, s, -OMe), 3.45 (1H, d, *J* 5.0 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.8, 136.6, 135.8, 132.8, 132.4, 129.4, 128.9, 127.9, 127.5, 86.2, 85.9, 65.1, 63.3, 55.0, 51.9, 49.8; ν_{max} (film) 3064, 2950, 2057, 1984, 1713, 1582, 1478, 1438, 1273, 1204, 1085, 1025, 743, 691, 610 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{23}H_{18}FeS_2O_5^+ Na)^+$, 516.9843; found 516.9860.

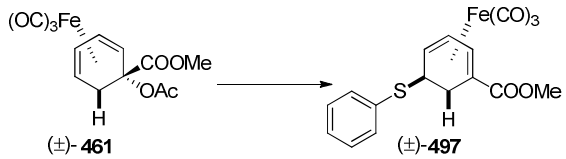
7.3.17 Synthesis of (–)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-methyl 2-acetoxy-3-dimethyl malonatecyclohexa-4,6-dienecarboxylate)iron(0), (467)



A solution of dimethyl malonate (87.6 µL), in THF (2 mL) was cooled to −78 ℃ and treated with *n*-BuLi (399 µL, 1.30 equiv), and left to stir for 15 min. Then reaction mixture were transferred via cannula into a solution of cationic solution of **383** in THF (10 mL), and left to stir for 48 h. The solution was quenched with NH_4Cl (5 mL), and washed with EtOAc (2 × 20 mL), brnie, dried ($MgSO_4$), and concentrated. Flash chromatography (40% EtOAc-hexane) gave product **467** as creamy foam (24 mg, 12%). R_f 0.30 [40:60 EtOAc-hexane]; δ_H (300 MHz, $CDCl_3$); 5.96 (1H, d, *J* 3.0, H-6), 5.45 (1H, t, *J* 5.0, H-5), 5.02 (1H, s, H-3*)*, 3.74 (3H, s, -O*Me*), 3.72 (3H, s, -O*Me*), 3.66 (3H, s, -COO*Me*), 3.47 (1H, d, *J* 7.0 Hz, H-2), 3.29 (1H, t, H-4), 2.07 (3H, s, OAc); δ_C (75.4 MHz, $CDCl_3$) 236.6 (3 × $Fe(CO)_3$), 168.1, 114.7, 90.6, 83.5, 70.6, 65.5, 58.9, 56.9, 53.0, 52.8, 52.0, 47.5,

21.0; v_{max} (film) 3463, 2956, 2060, 1982, 1731, 1435, 1369, 1235, 1196, 1163, 1101, 1029, 966, 909, 872, 802, 775, 687 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{18}H_{18}FeO_{11}+ Na)^+$, 489.0100; found 489.0045.

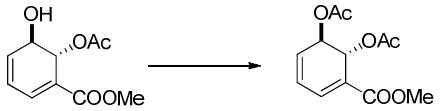
7.3.18 Synthesis of (±)-(4*S*)-Tricarbonyl(*η*^{4}-(2*R*,3*R*)-1-methyl 3-tiophenylcyclohexa-4,6-dienecarboxylate)iron(0), (497)



A solution of **461** (35 mg, 0.104 mmol, 1.00 equiv), in CH_2Cl_2 (1 mL) was treated with triphenylcarbenium tetrafluoroborate (36 mg, 0.109 mmol, 1.05 equiv), and left to stir for 1 h at room temperature, under nitrogen atmosphere. Then reaction mixture was cooled down to −12 ℃, and acetic acid (5.96 µL, 0.104 mmol, 1.00 equiv) was added, and left to stir for 1 h at 0 ℃. The solution was quenched with water (2 mL), and washed with CH_2Cl_2 (3 × 10 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (20% EtOAc-hexane) gave not stable product (±)-**497** as yellow foam (11.4 mg, 27%). R_f 0.20 [20:80 EtOAc-hexane]; δ_H (500 MHz, $CDCl_3$); 7.83 (2H, d, *J* 7.5, Ar), 7.68 (1H, t, *J* 14.0, 5.0 Hz, Ar-*p*ara-H), 7.58 (2H, t, *J* 15.0, 7.5 Hz, Ar-H*)*, 6.12 (1H, d, *J* 4.0 Hz*)*, 5.61 (1H, t, *J* 10.5, 5.0 Hz, H), 3.70 (3H, s, -O*Me*), 3.67 (1H, dt, *J* 11.0, 6.5, 3.0 Hz, H), 3.13 (1H, t, *J* 8.0, 3.5 Hz, H), 2.49 (1H, dd, *J* 16.0, 11.5 Hz, H), 1.89 (1H, dd, *J* 16.0, 3.0 Hz, H); δ_C (125.5 Hz, $CDCl_3$) 171.5, 137.9, 134.1, 129.5, 129.0, 90.0, 85.3, 64.6, 61.0, 52.1, 51.9, 25.8; v_{max} (film) 2964, 2924, 2853, 2059, 1981, 1709, 1464, 1447, 1381, 1306, 1274, 1254, 1192, 1145, 1084, 1026, 919, 886, 804, 763, 730, 695, 669, 649, 605 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{11}H_8FeO_5+ H)^+$, 276.9794; found 276.9797, m/z calcd for $(C_8H_8FeO_2+ H)^+$, 192.9947; found 192.9951.

7.3.19 Synthesis of Methyl trans-5,6-Diacetoxy-1,3-cyclohexadiene-1-carboxylate, (482)

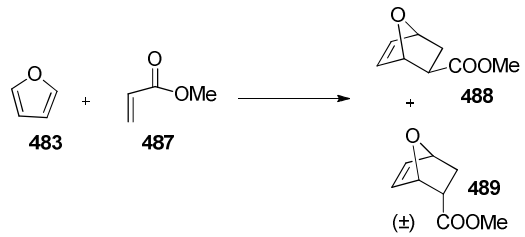
Synthesis from iron tricarbonyl complex



478 **482**

Acetylation of 478 to give 482. Compound **478** (4 mg, 0.018 mmol, 1.00 eq.) was dissolved in dry CH_2Cl_2 (2 mL) at 0 ℃ and Ac_2O (3.8 µL, 0.040 mmol, 2.0 eq.) was added portionwise, followed by Et_3N (8.4 µL, 0.060 mmol, 3.2 eq.). The reaction mixture was stirred at room temperature under an atmosphere of nitrogen for 24 h. The reaction mixture was transferred into separating funnel and extracted with EtOAc (4 × 10 mL), and water (10 mL) and the combined organic phases dried over Na_2SO_4, filtered and concentrated, followed by flash column chromatography (30% EtOAc-hexane) to give **482** as an white solid (3 mg, 63%) R_f 0.35 [30:70 EtOAc-Hexane]; $[\alpha]_D^{25}$ +440 (*c* 0.1, CH_2Cl_2); δ_H (500 MHz, $CDCl_3$); 7.28 (1H, d, *J* 6.0 Hz, H-6), 6.37 (1H, dd, *J* 9.5, 6.0 Hz, H-5), 6.29 (1H, dd, *J* 9.5, 6.0 Hz, H-4), 5.94 (1H, d, *J* 2.0 Hz, H-2), 5.29 (1H, dd, *J* 5.00, 2.00 Hz, H-3), 3.79 (3H, s, -COOMe), 2.05 (6H, s, 2 × -OC(O)CH_3); δ_C (125.8 MHz, $CDCl_3$) 169.6, 169.6, 165.8, 135.1, 129.1, 126.0, 125.4, 67.7, 65.9, 52.1, 21.0, 21.0; ν_{max} (film) 2955, 1742, 1717, 1594, 1437, 1370, 1295, 1221, 1084, 1022, 967, 749 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{12}H_{14}O_6Na_1)^+$, 277.0683; found 277.0773; for $(C_{24}H_{28}O_{12}Na_1)^+$, 531.1473; found 531.1581.

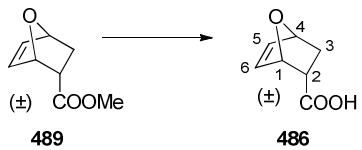
7.3.20 Synthesis of Methyl 7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylate, (489)



This was performed in accordance with a literature procedure.[297]

To a mixture of furan (6.00 g, 0.088 mmol, 3.00 eq.) and methyl acrylate (2.64 mL, 0.029 mmol, 1.00 eq.) 2 × 0.37 mL of BF_3-OEt_2 was added via syringe at −20 ℃ with stirring. Solution was stirred at this temp erature under nitrogen overnight. During the reaction, the solution colour changed to pale yellow. After evaporation of the excess reagents, the residue was poured into CH_2Cl_2 and washed successively with water (20 mL), $NaHCO_3$ (sat.), and brnie (20 mL), dried over $MgSO_4$, and concentrated in *vacuo* to give crude product purified further on silica-gel column chromatography (Hexane-EtOAc: 1:1) to give first fraction as an *endo*-product **489**, 263 mg, 6%, δ_H (100 MHz, CCl_4); 6.35 (1H, dd, *J* 6.0, 1.5 Hz, C5-H), 6.13 (1H, dd, *J* 6.0, 1.5 Hz, C6-H), 5.01 (1H, br d, *J* 5 Hz, C1-H), 4.89 (1H, br d, *J* 5 Hz, C4-H), 3.56 (3H, s), 2.96 (1H, q, *J* 4.5 Hz, C2-H), 2.00 (1H, ddd, *J* 11.5 10.5 Hz, C3-H), 1.50 (1H, dd, *J* 11.5, 4 Hz, C-H); Data in agreement with that previously reported.[313]

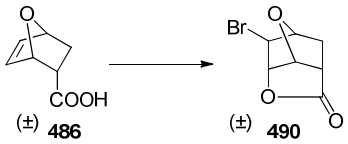
7.3.21 Synthesis of (±)-endo-7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid, (486)



This was performed in accordance with a literature procedure.[298] To racemic methyl ester product **489** was added 1 M NaOH (6 mL). The resulting mixture

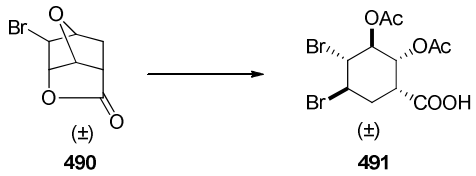
was stirred at room temp. for 23 h under nitrogen, before being acidified (conc. HCl, to Ph = 4.0) and extracted with DCM (8 × 20 mL). The organic phase was dried over $MgSO_4$, and evaporated under reduced pressure to give crystalline acid **486** (237.7 mg, 89%).m.p.=96–98 ℃, δ_H (60 MHz, $CDCl_3$); 8.81 (COOH), 6.45 (1H, dd, *J* 6.0, 2 Hz, C-H6), 6.28 (1H, dd, *J* 6.0, 2 Hz, C-H5), 5.06 (1H, br d, *J* 4, 2 Hz, C-H-4), 5.23 (1H, br d, *J* 4, 2 Hz, C-H1), 3.17 (1H, q, *J* 8, 4, 4 Hz, C-H2-*exo*), 2.13 (1H, m, C-H3-*exo*), 1.55 (1H, dd, *J* 10, 4 Hz, C-H3-*endo*);[314]
Data in agreement with that previously reported.[298,314]

7.3.22 Synthesis of Exo-9-Bromo-2,7-dioxabicyclo[4.2.1.0^{4,8}]nonan-3-one, (490)



This was performed in accordance with a literature procedure.[299]
Compound **486** (211.6 mg, 1.510 mmol, 1.00 eq.) was dissolved in water (6.5 mL) containing $NaHCO_3$ (152.2 mg, 1.812 mmol, 1.20 eq.). Bromine (85 µL, 1.661 mmol, 1.10 eq.) was added dropwise to this solution under vigorous agitation. Resultant mixture was stirred for 1 h, and precipitate was collected by filtration and washed with water thoroughly. Recrystalization of the crude product from EtOAc gave product **490** (269 mg, 81%) as prims: data in agreement with that previously reported.[299] δ_H (60 MHz, DMSO-d_6) 5.53 (1H, t, *J* 5 Hz, H-8), 4.95 (1H, d, *J* 5 Hz, H-1), 4.75 (1H, m, H-6), 4.37 (1H, s, H-9), 2.69 (1H, m, H-4), 2.00-2.29 (2H, m, C-5 methylene);

7.3.23 Synthesis of DL-(1,3,5/2,4)-2,3-Diacetoxy-4,5-dibromocyclohexane-1-carboxylic acid, (491)

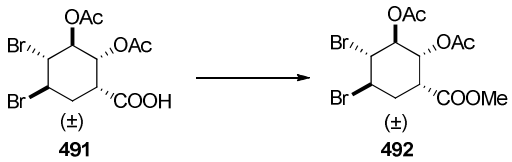


This was performed in accordance with a literature procedure.[300]

A mixture of **490** (268.7 mg, 1.227 mmol) and 33% hydrogen bromide in glacial acetic acid (2.5 mL) was heated in a sealed tube at 80 ℃ for 2 days. The cooled mixture was poured into ice-water, and the precipitate was collected and recrystallized from ethanol to give **491** (207 mg, 42%), as prims m.p.= 206-207 ℃; δ_H (90 MHz, CD_3OD); 2.04 (3H, s, OAc), 1.96 (3H, s, OAc).

Data in agreement with that previously reported.[300]

7.3.24 Synthesis of (±)-Methyl (1,3,5/2,4)-2,3-diacetoxy-4,5-dibromocyclohexane-1-carboxylate, (492)

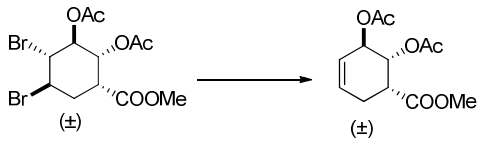


A mixture of **491** in 20 mL of MeOH-Benzene (1:1) was treated with slow addition of (trimethylsilyl)diazomethane (2.0 M solution in hexanes) when a yellow colour persisted (~ 2.75 mL) at room temperature.

The reaction mixture was stirred for 1h, and then concentrated under reduced pressure, dried *in vacuo* to give **492** (229.3 mg, 100%) as a light yellow oil, used immediately without purification. ^{1}H-NMR data (90 MHz); δ_H 3.70 (3H, s, Me),

2.66 (3H, s, OAc), 2.00 (3H, s, OAc). ^{1}H–NMR in agreement with that previously reported.[300]

7.3.25 Synthesis of (±)-Methyl (1,3/2)-2,3-diacetoxycyclohex-4-ene-1-carboxylate, (493)



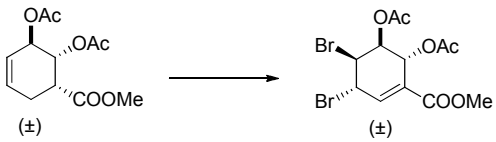
492 **493**

This was performed in accordance with a literature procedure.[300]

A mixture of **492** (229.3 mg, 0551 mmol, 1.00eq.), zinc powder (360.3 mg, 5.511 mmol, 10.00 eq.) and acetic acid (20 mL) was stirred vigorously at 70 ℃ for 1 h, and then the insoluble material was removed, and the filtrate concentrated. A solution of the residue in EtOAc (30 mL) was washed with 1M HCl and water. Dried over $MgSO_4$ and concentrated in *vacuo* to give crude of **493** (106.8 mg, 81%), as a prims m.p.= 67- 68.5 ℃; δ_H (90 MHz, CD_3OD); 5.87 (1H, dt, *J* 3.8, 9.6 Hz, H-4), 5.65-5.26 (3H, m, H-2,3,5), 3.67 (3H, s, Me), 2.93 (1H, dt, *J* 10.7, 8.6 Hz, H-1), 2.60-2.33 (2H, m, H-6,6'), 2.03 (3H, s, OAc), 2.00 (3H, s, OAc).

^{1}H NMR in agreement with that previously reported.[300]

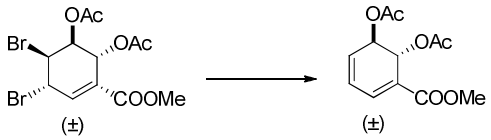
7.3.26 Synthesis of (±)-Methyl (2,5/3,4)-2,3-diacetoxy-4,5-dibromo-6-cyclohexene-1-carboxylate, (494)



493 **494**

This was performed in accordance with a literature procedure.[301] A mixture of **493** (106.8 mg, 0.417 mmol, 1.00 eq.), NBS (148.3 mg, 0.833 mmol, 2.00 eq.), AIBN (15mg), and carbon tetrachloride (4 mL), was refluxed under nitrogen atmosphere for 2h. Cooled reaction mixture was concentrated, and the residue absorbed on silica and was purified by silica-gel column chromatography with 2-butanone-toluene (1:20) as eluent to give three fractions, when the last one was desired product **494** (45 mg, 26%) as an oil, partially crystallized. No second column chromatography was performed. ^{1}H-NMR data in agreement with that previously reported.[301] m.p.= 115 – 116 ℃; δ_H (90 MHz, $CDCl_3$); 7.10 (1H, d, H-6), 6.03 (1H, d, H-2), 5.49 (1H, dd, *J* 6.5 Hz, H-3), 4.97 (1H, t, *J* 4 Hz, H-5), 4.57 (1H, dd, *J* 4.0, 2.7 Hz, H-4), 3.80 (3H, s, CO_2Me), 2.12 (3H, s, OAc), 2.07 (3H, s, OAc).

7.3.27 Synthesis of (±)-Methyl *trans*-5,6-Diacetoxy-1,3-cyclohexadiene-1-carboxylate, ((±)-482)

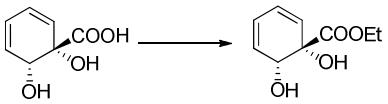


This was performed in accordance with a literature procedure.[301]

To a stirred solution of **494** (45 mg, 0.109 mmol, 1.00 eq.) in acetic acid (0.6 mL) was added zinc powder (28.4 mg, 0.4344 matom, 4.00 eq.) at room temperature. After 2 h, TLC (2-butanone-toulene 1:5) showed a disappearance of **494**. The reaction mixture was washed with water (10 mL), $NaHCO_3$ (sat.), and brnie (10 mL), dried over $MgSO_4$, concentrated and purified by silica gel column chromatography (30:70 EtOAc-Hexane) to give **482** (17.7 mg, 64%) as a white foam. R_f = 0.35, m.p.= 80 – 81 ℃; δ_H (90 MHz, $CDCl_3$); 7.28 (1H, dd, *J* 4.5, 1.5 Hz, H-2), 6.33 (2H, m, H-3 and H-4), 5.92 (1H, d, H-6), 5.27 (1H, dd, *J* 4.5, 1.7

Hz, H-5), 3.80 (3H, s, CO_2Me), 2.04 (6H, s, 2×OAc). ^{1}H–NMR data in agreement with that previously reported. [301]

7.3.28 Synthesis of (1*S*,2*R*)- ethyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate, (498)

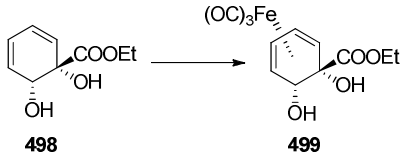


33 **498**

This was performed in accordance with a literature procedure.[243]

A mixture of diol acid **33** (1.03 g, 6.63 mmol, 1.00 eq.) and caesium fluoride (1.51 g, 9.94 mmol, 1.50 eq.) in DMF (15 mL) was stirred at room temperature for 2 min, followed by addition of ethyl iodide (0.799 mL, 9.94 mmol, 1.50 eq.). The reaction mixture was stirred for 23 h, then diluted with aqueous $NaHCO_3$ (15 mL) and extracted with EtOAc (3 × 15 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, then purified by chromatography (50:50 EtOAc-Hexane) to give **498** as a colourless oil, 846 mg (69%). R_f 0.37 (50:50 EtOAc-Petrol); $[\alpha]_D^{25}$ −140 (*c* 0.1, CH_2Cl_2); δ_H (500 MHz, $CDCl_3$): *δ* = 6.12 (1H, dd, *J* 9.5, 5.5 Hz, H-5), 5.93 (1H, dddd, *J* 9.5, 5.5, 3.0, 1.0 Hz, H-4), 5.80 (1H, ddt, *J* 9.5, 2.5, 1.0 Hz, H-3), 5.74 (1H, dd, *J* 9.5, 1.0 Hz, H-6), 4.83 (1H, d, *J* 5.0 Hz, H-2), 4.31 (2H, q, *J* 7.0 Hz, -C*H*$_2$CH$_3$), 3.67 (1H, s, C1-OH), 2.84 (1H, d, *J* 9.5 Hz, C2-OH), 1.32 (3H, t, *J* 7.0 Hz, -CH$_2$C*H*$_3$); δ_C (125.8 MHz, $CDCl_3$): *δ* = 175.3, 132.1, 126.7, 124.9, 122.8, 73.9, 71.0, 63.0, 14.3; FT-IR (neat): ν_{max} = 3448, 3049, 2983, 1727, 1446, 1408, 1369, 1246, 1169, 1078, 1039, 1019, 914, 858, 829, 754, 724, 693, 646 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_9H_{12}O_4Na_1)^+$, 207.0628; found 207.0748; for $(C_{18}H_{24}O_8Na_1)^+$, 391.1364; found 391.1374.

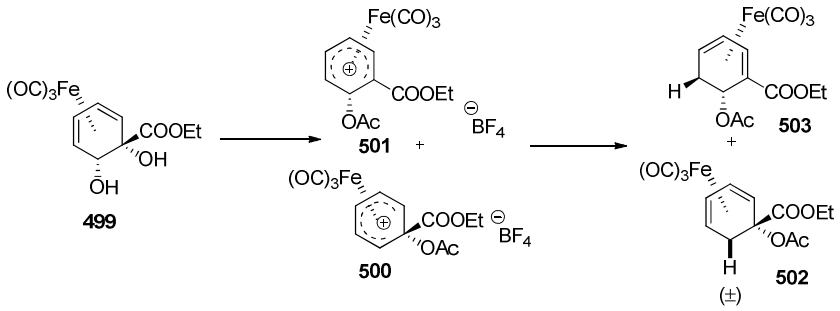
7.3.29 Synthesis of (–)-(3*S*)-Tricarbonyl(η^4-(1*S*,2*S*)-ethyl 1,2-dihydroxycyclohexa-3,5-dienecarboxylate)iron(0), (499)



498 **499**

To ester **498** (1.79 g, 5.52 mmol, 1.0 eq.) was added nonacarbonyldiiron (3.05 g, 8.28 mmol, 1.5 eq.). THF (200 mL) was added, and the reaction mixture was stirred at room temperature for 5 days. The reaction mixture was concentrated under reduced pressure (***caution! toxic pentacarbonyliron distilled over***) and the crude product was purified by chromatography (30:70 EtOAc-Petrol) to give **499** as a yellow foam, 1.09 g (61%). R_f 0.60 (30:70 EtOAc-Petrol); $[\alpha]_D^{25}$ -180 (*c* 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$): δ = 5.38-5.33 (2H, m, H-4,5), 4.22-4.15 (2H, m, -C*H*$_2$CH$_3$), 3.94 (1H, s, C1-OH), 3.88 (1H, d, *J* 5.0 Hz, H-2), 3.26 (1H, d, *J* 6.5 Hz, C2-OH), 3.21 (1H, dt, *J* 6.0, 2.0 Hz, H-3), 2.82 (1H, dd, *J* 6.0, 1.5 Hz, H-6), 1.27 (3H, t, *J* 7.0 Hz, -CH$_2$C*H*$_3$); δ_C (75.4 MHz, $CDCl_3$): δ = 210.2 (3 × Fe(CO)$_3$), 174.4, 84.5, 84.2, 77.2, 72.0, 67.6, 64.6, 62.7, 14.0; FT-IR (neat): ν_{max} = 3401.5, 2991, 2905, 2051, 1960, 1720, 1574, 1446, 1377, 1297, 1233, 1175, 1133, 1063, 1026, 936, 866, 831, 737 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{12}H_{12}FeO_7Na_1)^+$, 346.9825; found 346.9926, $(C_{24}H_{24}Fe_2O_{14}Na_1)^+$, 670.9758; found 670.9853.

7.3.30 Synthesis of (±)-(3*S*)-Tricarbonyl(η^4-(1*S*)-ethyl 1-acetoxycyclohexa-3,5-dienecarboxylate)iron(0), (502) and (–)-(4*S*)-Tricarbonyl(η^4-(2*S*)-1-ethyl 2-acetoxycyclohexa-4,6-dienecarboxylate)iron(0), (503)



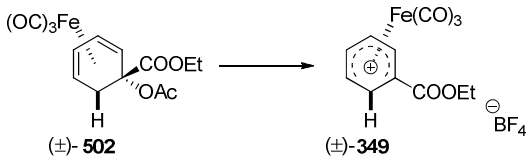
Tetrafluoroboric acid diethyl etherate (319 µL, 2.33 mmol 4.00 eq.) was added to a stirred solution of complex **499** (189 mg, 0.583 mmol, 1.00 eq.) in acetic anhydride (5.8 mL) at −10 °C and stirred at this temperature for 1 h. To the reaction mixture, pre-cooled Et_2O was added (60 mL) dropwise, giving a light yellow precipitate. This was filtered by suction and washed with cold Et_2O (3 × 5 mL). The crude cation mixture was redissolved in MeCN at 0 °C, and $NaBH_4$ (111 mg, 2.91 mmol, 5.00 eq.) was added in one portion. The reaction mixture allowed to warm to room temperature and was stirred for 18 h, then quenched by addition of H_2O. The product was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the crude product was purified by chromatography (10:90 EtOAc-Hexane) to give (±)-**502** as a yellow foam, 80.3 mg (39%). R_f 0.25 (10:90 EtOAc-Hexane); δ_H (500 MHz, $CDCl_3$): δ = 5.47 (1H, t, J 5.5 Hz, H-4), 5.36 (1H, t, J 5.5 Hz, H-5), 4.18-4.07 (2H, m, -CH_2CH_3), 3.20-3.17 (1H, m, H-3), 3.08 (1H, d, J 6.5 Hz, H-6), 2.73 (1H, d, J 16.0 Hz, H-2), 2.09 (3H, s, -OC(O)CH_3), 1.92 (1H, dd, J 16.0, 3.5 Hz, H-2); 1.22 (3H, t, *J* 7.0 Hz, -CH_2CH_3); δ_C (125.8 MHz, $CDCl_3$): δ = 210.6 (3 × $Fe(CO)_3$), 171.3, 170.1, 87.1, 82.3, 81.5, 61.8, 61.6, 60.5, 39.9, 21.0, 14.6; FT-IR (neat): ν_{max} = 2985, 2051,

1969, 1740, 1427, 1370, 1251, 1196, 1097, 1054, 1014, 954, 869 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7Na_1)^+$, 372.9986; found 372.9996.

Second product **503** was isolated as a yellow foam, 10.9 mg (5%). R_f 0.14 (10:90 EtOAc- Hexane); $[\alpha]_D^{25}$ +120 (*c* 0.1, CH_2Cl_2); δ_H (250 MHz, $CDCl_3$): δ = 5.95 (1H, dd, *J* 4.5, 1.5 Hz, H-6), 5.52 (1H, t, *J* 5.5 Hz, H-5), 5.04 (1H, d, *J* 6.5 Hz, H-2), 4.24-4.02 (2H, m, $-CH_2CH_3$), 3.22-3.17 (1H, m, H-4), 2.10-2.00 (1H, m, H-3) 2.06 (3H, s, $-OC(O)CH_3$), 1.57 (1H, ddd, *J* 16.0, 4.5, 1.0 Hz, H-3), 1.24 (3H, t, *J* 7.0 Hz, $-CH_2CH_3$); δ_C (75.4 MHz, $CDCl_3$): δ = 209.5 (3 × $Fe(CO)_3$), 171.2, 170.1, 90.4, 84.4, 68.5, 68.2, 61.0, 58.6, 34.3, 21.2, 14.1; FT-IR (neat): ν_{max} = 2925, 2057, 1981, 1739, 1710, 1505, 1448, 1368, 1240, 1207, 1098, 1043, 871, 752, 715, 612 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7Na_1)^+$, 372.9986; found 372.9974.

NMR data for this racemic compound is in agreement with a recent enantiopure Synthesis of 5.[225]

7.3.31 Synthesis of (±)-tricarbonyl 1-ethyl cyclohexa-3,5-dienecarboxylate]iron tetrafluoroborate, (349)

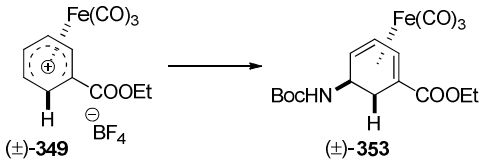


Deacetoxylation to give cation (±)-349. Iron complex **(±)-502** (51.5 mg, 0.147 mmol) was dissolved in dry CH_2Cl_2 (3 mL) at −12 ℃ and HBF_4-eterate (30.2 µL, 0.220 mmol, 1.50 eq.) was added portionwise. The reaction mixture was stirred at this temperature under an atmosphere of nitrogen for 1 h. The reaction mixture was added to cold Et_2O (50 mL) to give a precipitate that was isolated by filtration, washed with Et_2O and dried under vacuum affording **(±)-349** as a pale yellow powder, 55.5 mg (100%); δ_H (300 MHz, CD_3CN); 7.38 (1H, t, *J* 5.0 Hz),

6.57 (1H, d, *J* 5.5 Hz), 5.91 (1H, t, *J* 5.5 Hz), 4.70 (1H, t, *J* 6.5 Hz), 4.26 (1H, q, *J* 7.0 Hz), 3.27 (1H, dd, *J* 15.5, 6.5 Hz), 1.96-1.86 (1H, m), 1.28 (1H, t, *J* 7.0 Hz); δ_C (75.4 MHz, CD_3CN): 167.6, 105.1, 103.0, 91.3, 71.8, 63.9, 56.0, 24.2, 14.1; HRMS (+ve ESI-TOF) m/z calcd for $(C_{12}H_{11}FeO_5)^+$, 290.9951; found 290.9925.

NMR data for this racemic compound is in agreement with a recent enantiopure Synthesis of 5.[225]

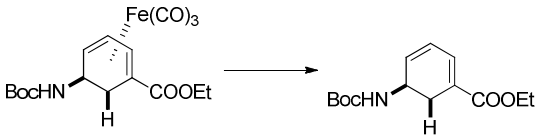
7.3.32 Synthesis of (±)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-ethyl 3-(*tert*-Butoxycarbonylamino)cyclohexa-4,6-dienecarboxylate)iron(0), (353)



Formation of (±)-353. To a suspension of $[\eta^5]^+$ complex **(±)-349** (51.5 g, 0.1471 mmol, 1.00 eq.) in dry CH_2Cl_2 (3 mL) and *tert*-butyl carbamate (34.5 mg, 0.294 mmol, 2.00 eq.) at 0 ℃ was added dropwise di*iso*propylethyl amine (38.5 µL, 1.50 eq.). The reaction mixture stirred on ice for 30 min before being allowed to warm to room temperature. Left to stir under nitrogen for 23 h. The reaction mixture was further stirred for 23 h, then quenched by addition of water, transferred to a separating funnel and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by column chromatography (20:80 EtOAc-Petrol) to give **(±)-353** as a yellow oil, 48.2 mg (82%). R_f 0.59 [20% EtOAc-hexane]; δ_H (300 MHz, $CDCl_3$); 6.20 (1H, d, *J* 4.0 Hz), 5.39 (1H, dd, *J* 6.0, 4.5 Hz), 4.40-4.17 (2H, m), 4.21-4.03 (2H, m), 3.27 (1H, br s), 2.84 (1H, dd, *J* 15.0, 11.0 Hz), 1.41 (9H, s), 1.25 (3H, t, *J* 7.0 Hz), 1.16 (1H, dd, *J* 15.0, 3.0 Hz);

δ_C (75.4 MHz, $CDCl_3$) 171.8, 155.1, 90.0, 84.2, 79.9, 62.6, 61.0, 59.6, 49.5, 31.0, 28.5, 14.2; Data in agreement with those previously reported.[315]

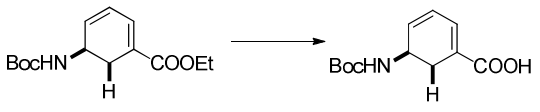
7.3.33 Synthesis of (±)-Ethyl 5-(*tert*-Butoxycarbonylamino)-cyclohexa-1,3-diene-1-carboxylate, (354).



(±)-**353** (±)- **354**

Formation of (±)-354. To a solution of the iron complex **(±)-353** (48.9 mg, 0.120 mmol) in EtOH (20 mL) on an ice bath at 0 ℃ was ad ded aqueous hydrogen peroxide (30%, 8.3 mL), followed by the dropwise addition of 1M NaOH (7.23 mL) and the reaction mixture was stirred on ice under a nitrogen atmosphere for 5 min. The reaction was diluted with brine (50 mL) and the product extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated, affording **(±)-354** as a light yellow oil 22.6 mg (71%); δ_H (400 MHz, $CDCl_3$); 7.04 (1H, d, *J* 4.0, 1.0 Hz), 6.19-6.10 (2H, m), 4.64 (1H, br s), 4.43 (1H, br s), 4.22 (2H, q, *J* 14.0, 7.0 Hz), 2.76-2.62 (1H, m), 1.43 (9H, s), 1.30 (1H, t, *J* 7.0 Hz); NMR data for this racemic compound is in agreement with a recent enantiopure synthesis of 9.[315]

7.3.34 Synthesis of (±)-5-*tert*-Butoxycarbonylamino-cyclohexa-1,3-dienecarboxylic Acid, (278)

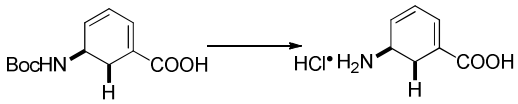


(±)- **354** (±)-**278**

Formation of (±)-278. To a suspension of **354** in methanol (2 mL) at room temperature was added 2 M NaOH (1 mL) and left to stir for 2 h 50 min. The solution was acidified with 2 M HCl, and extracted with DCM (5 × 20 mL), dried over $MgSO_4$, concentrated on *vacuo* to give racemic **(±)-278** without further purification as a white solid (13.5 mg, 67%); δ_H (300 MHz, $CDCl_3$); 7.17 (1H, m), 6.20 (2H, m), 4.69-4.67 (1H, br, N*H*), 4.47-4.45 (1H, br), 2.70 (2H, m), 1.43 (9H, s); HRMS (+ve ESI-TOF) m/z calcd for $(C_{12}H_{17}FeO_4Na_1)^+$, 238.1079; found 238.1075.

NMR data for this racemic compound is in agreement with a recent enantiopure Synthesis of 5.[203]

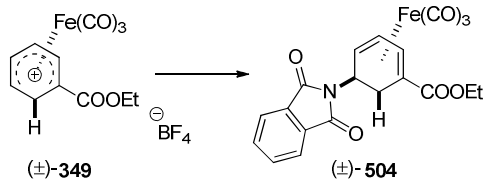
7.3.35 Synthesis of (±)-5-amino-cyclohexa-1,3-dienecarboxylic acid, (279)



(±)- **278** (±)- **279**

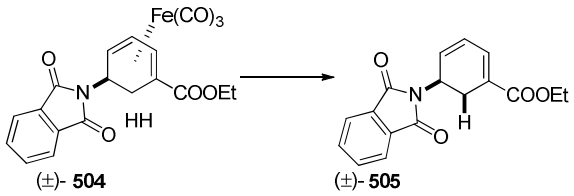
Formation of (±)-279. A solution of HCl/dioxane (2 mL, 4 *N* HCl) was added to the racemic **(±)-278** (13.5 mg, 0.056 mmol) under nitrogen, cooled on an ice bath to 0 ℃, with stirring. Allowed to warm up the reac tion mixture to room temperature over 1h. The reaction mixture was concentrated under high pressure, dried in *vacuo*, followed by flash column chromatography (silica: 8:3:1, chloroform-methanol-water) to give racemic **(±)-279** as a white solid, mp=195-199 ℃ (lit. [316] mp=198-200 ℃), (7.5 mg, 96%); δ_H (400 MHz, D_2O); 6.76 (1H, d, *J* 5.5 Hz), 6.41 (1H, dd, *J* 9.5, 5.5 Hz), 6.00 (1H, dd, *J* 9.5, 5.0 Hz), 4.04 (1H, dd, *J* 12.0, 6.0 Hz), 2.72-2.69 (2H, m); δ_C (100.6 MHz, D_2O) 174.8, 131.8, 129.4, 128.0, 123.4, 44.4, 27.2; HRMS (-ve ESI-TOF) m/z calcd for $(C_7H_8NO_2)^+$, 138.0555; found 138.0569.

7.3.36 Synthesis of (±)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-ethyl 3-(1,3-dioxoisoindolin-2-yl)cyclohexa-4,6-dienecarboxylate)iron(0), (504)



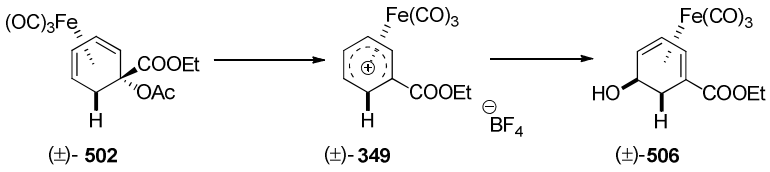
Formation of (±)-504. To a suspension of $[\eta^5]^+$ complex **(±)-349** (78.2 g, 0.2233 mmol) and potassium phthalimide (124 mg, 0.699 mmol, 3.00 eq.) in CH_2Cl_2 (4.4 mL) was cooled to 0 ℃. Di *iso*propylethyl amine (42.7 µL, 0.246 mmol, 1.10 eq.) was added dropwise and the reaction mixture was stirred at 0 ℃ for 30 min before being allowed to warm to room temperature. The reaction mixture was stirred for 23 h, then quenched by addition of water, transferred to a separating funnel and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure, then purified by column chromatography (15:85 EtOAc-Petrol) to give (±)-**504** as a yellow solid, 70.8 mg (73%). R_f 0.73 (15:85 EtOAc-Petrol); mp: 124-125 ℃; δ_H (400 MHz, $CDCl_3$): 7.79 (2H, dd, *J* 5.5, 3.0 Hz, Ar-H), 7.69 (2H, dd, *J* 5.5, 3.0 Hz, Ar-H), 6.33 (1H, d, *J* 4.5 Hz, H-6), 5.59 (1H, t, *J* 5.5 Hz, H-5), 4.90 (1H, dt, *J* 11.5, 3.5 Hz, H-3), 4.24-4.08 (2H, m, -C*H*$_2$CH$_3$), 2.91 (1H, dd, *J* 5.0, 3.5 Hz, H-4), 2.78 (1H, dd, *J* 15.0, 11.5 Hz, H-2), 1.84 (1H, dd, *J* 15.0, 4.0 Hz, H-2), 1.26 (3H, t, *J* 7.0 Hz, -CH$_2$C*H*$_3$); δ_C (100.6 MHz, $CDCl_3$): 171.6, 167.7, 134.0, 131.7, 123.2, 89.5, 85.7, 60.8, 60.0, 58.2, 48.3, 26.3, 14.1; ν_{max} (film) 2982, 2057, 1982, 1774, 1708, 1468, 1382, 1354, 1327, 1270, 1249, 1117, 1083, 1042, 881, 716, 649, 606 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{20}H_{15}FeNO_7Na_1)^+$, 460.0091; found 460.0104.

7.3.37 Synthesis of (±)-(*S*)-ethyl 5-(1,3-dioxoisoindolin-2-yl)cyclohexa-1,3-dienecarboxylate, (505)



To a solution of the iron complex **(±)-504** (38 mg, 0.0869 mmol, 1.00 eq.) in EtOH (17 mL) at 0 ℃ was added aqueous hydrogen peroxide (30%, 6.0 mL), followed by the dropwise addition of aqueous NaOH (1.0 M, 5.2 mL). The reaction mixture was stirred for 5 min. The reaction was diluted with brine (50 mL) and the product extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered. The filtrate was concentrated under reduced pressure, affording **(±)-505** as a light yellow foam, mp= 124-125 ℃, 19.8 mg (77 %). δ_H (400 MHz, $CDCl_3$); 7.84 (2H, dd, *J* 5.5, 3.0 Hz), 7.74 (2H, dd, *J* 5.5, 3.0 Hz), 7.09 (1H, m), 6.23 (1H, ddd, *J* 9.5, 5.5, 3.0 Hz), 6.00 (1H, dd, *J* 9.5, 3.0 Hz), 5.23 (1H, ddm, *J* 13.0, 10.0 Hz), 4.22 (2H, q, *J* 14.0, 7.0 Hz), 2.93 (1H, dt, *J* 17.5, 15.0, 2.5 Hz); 2.81 (1H, dd, *J* 17.0, 10.0, Hz); 1.30 (3H, t, *J* 14.0, 7.0 Hz); δ_C (100.6 MHz, $CDCl_3$) 167.9, 166.8, 134.5, 132.8, 131.7, 131.6, 127.8, 125.0, 123.8, 60.8, 46.1, 26.6, 14.4;
NMR data for this racemic compound is in agreement with previously reported.[224]

7.3.38 Synthesis of (±)-(4*S*)-Tricarbonyl(η^4-(2*S*,3*R*)-1-ethyl 3-hydroxylcyclohexa-4,6-dienecarboxylate)iron(0), (506)



(±)- **502** (±)- **349** (±)-**506**

To a suspension of $[\eta^5]^+$ complex **(±)-502** (15 mg, 0.042 mmol, 1.00 eq.) in dry CH_2Cl_2 (2 mL) at −12 ℃ and HBF_4-etherate (8.8 µL, 0.064 mmol, 1.50 eq.) was added portionwise. The reaction mixture was stirred at this temperature under an atmosphere of nitrogen for 1 h. To this reaction mixture, cooled on an ice bath to 0 ^oC, and then *tert*-butyl carbamate (10.0 mg) was added, The reaction mixture stirred on ice for 30 min before allowing it to warm to room temperature. Left to stir under nitrogen for 1h. The reaction mixture was transferred into separating funnel and extracted with water (5 mL), and CH_2Cl_2 (5 × 10mL) and the combined organic phases dried over $MgSO_4$, filtered and concentrated, followed by flash column chromatography (20:80 EtOAc-Hexane) to give racemic **(±)-506** as an yellow oil 10.5 mg (80%); R_f 0.24 [20:80 EtOAc-Petrol]; (500 MHz, $CDCl_3$); 6.28 (1H, d, *J* 4.5 Hz), 5.50 (1H, t, *J* 5.5 Hz), 4.45 (1H, d, *J* 4.5 Hz), 4.22-4.08 (2H, m, -C*H*$_2$Me), 3.18 (1H, t, *J* 5.0 Hz), 2.82 (1H, dd, *J* 15.5, 10.0 Hz), 1.59 (1H, s), 1.37 (1H, dd, *J* 15.5, 2.5 Hz), 1.26 (3H, t, *J* 7.0 Hz, -CH_2*CH*$_3$); δ_C (125.8 MHz, $CDCl_3$) 210.5 (3 × $Fe(CO)_3$), 171.8, 90.5, 84.5, 69.9, 63.8, 61.0, 58.6, 32.8, 30.5, 14.2; ν_{max} (film) 2980, 2057, 1984, 1706, 1281, 1245, 1085, 1024, 609 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{12}H_{12}FeO_6Na_1)^+$, 330.9876; found 330.9981.

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Appendix 1

Crystal data of new compounds

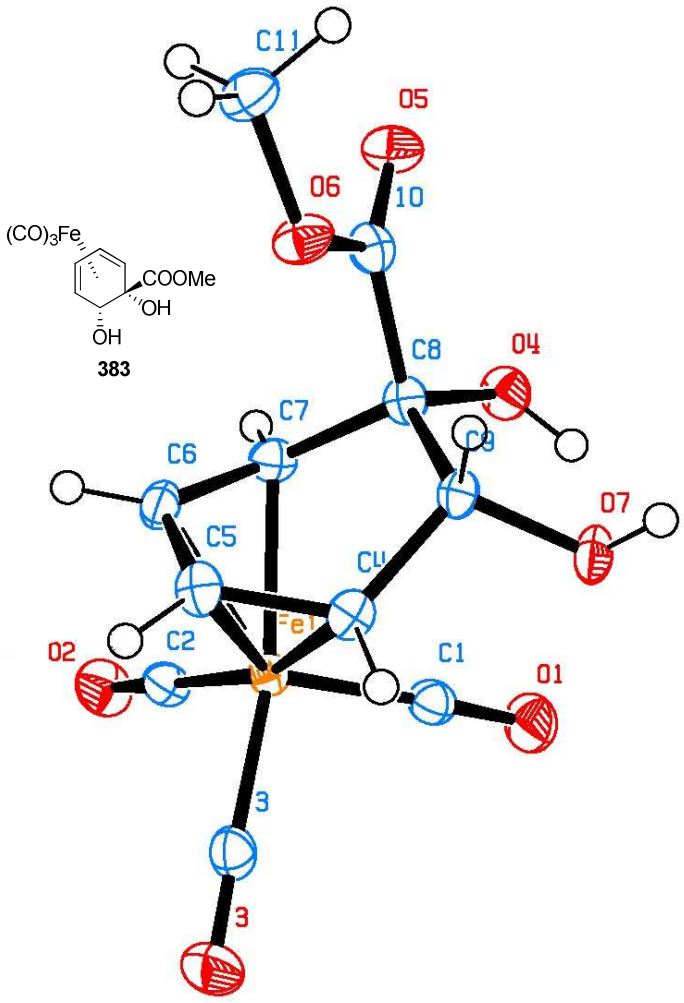


Figure 13

ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **383**

Table 6 Crystal data and structure refinement for **383.**

Identification code	k08sel1
Empirical formula	C11 H10 Fe O7
Formula weight	310.04
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P212121
Unit cell dimensions	a = 8.0220(1)Å α = 90°
	b = 8.1780(1)Å β = 90°
	c = 18.1270(3)Å γ = 90°

Volume	1189.20(3) $Å^3$
Z	4
Density (calculated)	1.732 Mg/m^3
Absorption coefficient	1.295 mm^{-1}
F(000)	632
Crystal size	0.20 x 0.30 x 0.40 mm
Theta range for data collection	3.56 to 29.13 °.
Index ranges	-10<=h<=10; -11<=k<=11; -24<=l<=24
Reflections collected	25065
Independent reflections	3187 [R(int) = 0.0524]
Reflections observed (>2σ)	2889
Data Completeness	0.997
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.68 and 0.63
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3187 / 4 / 193
Goodness-of-fit on F^2	1.108
Final R indices [I>2σ(I)]	R1 = 0.0259 wR2 = 0.0588
R indices (all data)	R1 = 0.0349 wR2 = 0.0622
Absolute structure parameter	-0.034(14)
Largest diff. peak and hole	0.644 and -0.856 $eÅ^{-3}$

Notes: H4-H7 located and refined at a distance of 0.98Å from the relevant parent atoms. Intramolecular and intermolecular hydrogen bonding present.

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O4-H4A	0.840	1.994	123.58	2.556	O7
O7-H7A	0.840	1.989	156.40	2.780	O5 [-x, y+1/2, -z+3/2]

Table 7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 383. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	-29(1)	9595(1)	5514(1)	16(1)
O(1)	-3424(2)	10047(2)	6086(1)	34(1)
O(2)	92(2)	6016(2)	5503(1)	32(1)
O(3)	-921(2)	9774(2)	3946(1)	38(1)
O(4)	-608(2)	10934(2)	7404(1)	24(1)
O(5)	2374(2)	11216(2)	8081(1)	26(1)
O(6)	3480(2)	12350(2)	7068(1)	25(1)
O(7)	-1291(2)	13153(2)	6458(1)	23(1)
C(1)	-2097(3)	9887(2)	5875(1)	23(1)
C(2)	28(2)	7402(2)	5502(1)	22(1)
C(3)	-549(2)	9712(2)	4549(1)	24(1)

C(4)	691(2)	12061(2)	5599(1)	19(1)
C(5)	2067(2)	11041(2)	5421(1)	21(1)
C(6)	2347(2)	9749(2)	5918(1)	20(1)
C(7)	1213(2)	9675(2)	6522(1)	20(1)
C(8)	775(2)	11240(2)	6938(1)	19(1)
C(9)	410(2)	12655(2)	6381(1)	18(1)
C(10)	2262(2)	11620(2)	7441(1)	20(1)
C(11)	5024(3)	12640(2)	7460(1)	27(1)

Table 8 Bond lengths [Å] and angles [^{o}] for 383.

Fe(1)-C(2)	1.7942(17)	Fe(1)-C(1)	1.799(2)
Fe(1)-C(3)	1.8025(19)	Fe(1)-C(6)	2.0459(18)
Fe(1)-C(5)	2.0628(18)	Fe(1)-C(7)	2.0813(17)
Fe(1)-C(4)	2.1037(17)	O(1)-C(1)	1.139(2)
O(2)-C(2)	1.135(2)	O(3)-C(3)	1.134(2)
O(4)-C(8)	1.417(2)	O(4)-H(4A)	0.8400
O(5)-C(10)	1.210(2)	O(6)-C(10)	1.329(2)
O(6)-C(11)	1.448(3)	O(7)-C(9)	1.4312(19)
O(7)-H(7A)	0.8400	C(4)-C(5)	1.420(3)
C(4)-C(9)	1.515(2)	C(4)-H(4)	0.940(15)
C(5)-C(6)	1.406(3)	C(5)-H(5)	0.959(14)
C(6)-C(7)	1.425(3)	C(6)-H(6)	0.923(15)
C(7)-C(8)	1.526(2)	C(7)-H(7)	0.959(14)
C(8)-C(10)	1.532(2)	C(8)-C(9)	1.564(2)
C(9)-H(9)	1.0000	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(2)-Fe(1)-C(1)	99.26(9)	C(2)-Fe(1)-C(3)	92.67(8)
C(1)-Fe(1)-C(3)	97.63(9)	C(2)-Fe(1)-C(6)	92.44(9)
C(1)-Fe(1)-C(6)	136.16(7)	C(3)-Fe(1)-C(6)	124.02(8)
C(2)-Fe(1)-C(5)	123.46(8)	C(1)-Fe(1)-C(5)	134.85(8)
C(3)-Fe(1)-C(5)	94.51(8)	C(6)-Fe(1)-C(5)	40.01(8)
C(2)-Fe(1)-C(7)	91.76(7)	C(1)-Fe(1)-C(7)	96.80(8)
C(3)-Fe(1)-C(7)	164.02(8)	C(6)-Fe(1)-C(7)	40.39(7)
C(5)-Fe(1)-C(7)	70.33(7)	C(2)-Fe(1)-C(4)	162.22(8)
C(1)-Fe(1)-C(4)	95.71(8)	C(3)-Fe(1)-C(4)	94.81(8)
C(6)-Fe(1)-C(4)	70.03(8)	C(5)-Fe(1)-C(4)	39.85(7)
C(7)-Fe(1)-C(4)	76.93(7)	C(8)-O(4)-H(4A)	109.5
C(10)-O(6)-C(11)	116.91(14)	C(9)-O(7)-H(7A)	109.5
O(1)-C(1)-Fe(1)	177.98(17)	O(2)-C(2)-Fe(1)	178.58(18)
O(3)-C(3)-Fe(1)	178.09(18)	C(5)-C(4)-C(9)	121.11(16)
C(5)-C(4)-Fe(1)	68.52(10)	C(9)-C(4)-Fe(1)	109.58(11)
C(5)-C(4)-H(4)	116.0(13)	C(9)-C(4)-H(4)	114.1(13)
Fe(1)-C(4)-H(4)	119.9(13)	C(6)-C(5)-C(4)	114.85(16)
C(6)-C(5)-Fe(1)	69.35(11)	C(4)-C(5)-Fe(1)	71.63(10)
C(6)-C(5)-H(5)	120.1(13)	C(4)-C(5)-H(5)	123.9(12)
Fe(1)-C(5)-H(5)	118.2(12)	C(5)-C(6)-C(7)	114.93(17)
C(5)-C(6)-Fe(1)	70.64(10)	C(7)-C(6)-Fe(1)	71.14(10)
C(5)-C(6)-H(6)	120.8(13)	C(7)-C(6)-H(6)	124.2(13)
Fe(1)-C(6)-H(6)	125.0(13)	C(6)-C(7)-C(8)	119.43(16)
C(6)-C(7)-Fe(1)	68.47(10)	C(8)-C(7)-Fe(1)	110.51(11)
C(6)-C(7)-H(7)	121.1(12)	C(8)-C(7)-H(7)	112.9(11)
Fe(1)-C(7)-H(7)	116.2(12)	O(4)-C(8)-C(7)	109.07(14)
O(4)-C(8)-C(10)	106.93(13)	C(7)-C(8)-C(10)	106.56(14)
O(4)-C(8)-C(9)	111.66(14)	C(7)-C(8)-C(9)	110.12(14)
C(10)-C(8)-C(9)	112.30(14)	O(7)-C(9)-C(4)	108.94(14)
O(7)-C(9)-C(8)	109.03(13)	C(4)-C(9)-C(8)	109.79(13)
O(7)-C(9)-H(9)	109.7	C(4)-C(9)-H(9)	109.7
C(8)-C(9)-H(9)	109.7	O(5)-C(10)-O(6)	123.76(16)
O(5)-C(10)-C(8)	124.91(16)	O(6)-C(10)-C(8)	111.16(14)
O(6)-C(11)-H(11A)	109.5	O(6)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	O(6)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 9 Anisotropic displacement parameters ($Å^2$ x 10^3) for 383. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	18(1)	14(1)	17(1)	1(1)	1(1)	0(1)
O(1)	22(1)	43(1)	37(1)	-7(1)	5(1)	-3(1)
O(2)	43(1)	17(1)	34(1)	-3(1)	-1(1)	0(1)
O(3)	48(1)	46(1)	21(1)	1(1)	-2(1)	10(1)
O(4)	20(1)	28(1)	25(1)	1(1)	5(1)	-4(1)
O(5)	27(1)	29(1)	21(1)	4(1)	-2(1)	-8(1)
O(6)	18(1)	32(1)	24(1)	6(1)	-2(1)	-7(1)
O(7)	18(1)	19(1)	33(1)	-4(1)	3(1)	5(1)
C(1)	24(1)	22(1)	21(1)	-2(1)	-2(1)	-1(1)
C(2)	25(1)	20(1)	19(1)	-1(1)	-1(1)	0(1)
C(3)	27(1)	22(1)	24(1)	0(1)	3(1)	4(1)
C(4)	20(1)	15(1)	22(1)	4(1)	1(1)	-1(1)
C(5)	20(1)	19(1)	24(1)	0(1)	5(1)	-3(1)
C(6)	16(1)	19(1)	26(1)	-3(1)	-1(1)	3(1)
C(7)	23(1)	16(1)	20(1)	2(1)	-3(1)	0(1)
C(8)	18(1)	18(1)	20(1)	1(1)	3(1)	-2(1)
C(9)	17(1)	15(1)	22(1)	0(1)	1(1)	2(1)
C(10)	23(1)	15(1)	23(1)	-1(1)	2(1)	-2(1)
C(11)	19(1)	32(1)	28(1)	3(1)	-2(1)	-2(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 383

Atom	x	y	z	U(eq)
H(4A)	-1421	11504	7266	57(9)
H(7A)	-1328	14102	6634	33(6)
H(9)	1163	13602	6486	22
H(11A)	5820	13183	7132	40
H(11B)	5489	11594	7626	40
H(11C)	4807	13338	7889	40
H(4)	370(30)	12810(20)	5234(10)	30(6)
H(5)	2640(20)	11060(30)	4957(8)	19(5)
H(6)	3180(20)	8990(20)	5833(10)	18(5)
H(7)	1130(20)	8710(20)	6823(10)	15(5)

Table 11 Dihedral angles [°] for 383

Atom1 - Atom2 - Atom3 - Atom4	Dihedral
C(2) - Fe(1) - C(1) - O(1)	-59(5)
C(3) - Fe(1) - C(1) - O(1)	35(5)
C(6) - Fe(1) - C(1) - O(1)	-163(5)
C(5) - Fe(1) - C(1) - O(1)	139(5)
C(7) - Fe(1) - C(1) - O(1)	-152(5)
C(4) - Fe(1) - C(1) - O(1)	131(5)
C(1) - Fe(1) - C(2) - O(2)	-122(7)
C(3) - Fe(1) - C(2) - O(2)	139(7)
C(6) - Fe(1) - C(2) - O(2)	15(7)
C(5) - Fe(1) - C(2) - O(2)	42(7)
C(7) - Fe(1) - C(2) - O(2)	-25(7)
C(4) - Fe(1) - C(2) - O(2)	25(7)
C(2) - Fe(1) - C(3) - O(3)	77(5)
C(1) - Fe(1) - C(3) - O(3)	-22(5)
C(6) - Fe(1) - C(3) - O(3)	172(5)
C(5) - Fe(1) - C(3) - O(3)	-159(5)

C(7) - Fe(1) - C(3) - O(3)	-177(100)
C(4) - Fe(1) - C(3) - O(3)	-119(5)
C(2) - Fe(1) - C(4) - C(5)	23.2(3)
C(1) - Fe(1) - C(4) - C(5)	170.53(11)
C(3) - Fe(1) - C(4) - C(5)	-91.29(12)
C(6) - Fe(1) - C(4) - C(5)	33.24(10)
C(7) - Fe(1) - C(4) - C(5)	74.86(11)
C(2) - Fe(1) - C(4) - C(9)	-93.5(2)
C(1) - Fe(1) - C(4) - C(9)	53.83(13)
C(3) - Fe(1) - C(4) - C(9)	152.01(13)
C(6) - Fe(1) - C(4) - C(9)	-83.47(12)
C(5) - Fe(1) - C(4) - C(9)	-116.70(17)
C(7) - Fe(1) - C(4) - C(9)	-41.85(11)
C(9) - C(4) - C(5) - C(6)	44.8(2)
Fe(1) - C(4) - C(5) - C(6)	-55.71(14)
C(9) - C(4) - C(5) - Fe(1)	100.55(15)
C(2) - Fe(1) - C(5) - C(6)	-44.94(13)
C(1) - Fe(1) - C(5) - C(6)	113.41(13)
C(3) - Fe(1) - C(5) - C(6)	-141.15(11)
C(7) - Fe(1) - C(5) - C(6)	33.68(11)
C(4) - Fe(1) - C(5) - C(6)	126.75(15)
C(2) - Fe(1) - C(5) - C(4)	-171.69(10)
C(1) - Fe(1) - C(5) - C(4)	-13.35(16)
C(3) - Fe(1) - C(5) - C(4)	92.10(12)
C(6) - Fe(1) - C(5) - C(4)	-126.75(15)
C(7) - Fe(1) - C(5) - C(4)	-93.07(11)
C(4) - C(5) - C(6) - C(7)	-0.3(2)
Fe(1) - C(5) - C(6) - C(7)	-57.24(14)
C(4) - C(5) - C(6) - Fe(1)	56.93(14)
C(2) - Fe(1) - C(6) - C(5)	143.85(11)
C(1) - Fe(1) - C(6) - C(5)	-110.08(13)
C(3) - Fe(1) - C(6) - C(5)	48.98(14)
C(7) - Fe(1) - C(6) - C(5)	-126.30(16)
C(4) - Fe(1) - C(6) - C(5)	-33.11(10)
C(2) - Fe(1) - C(6) - C(7)	-89.84(12)
C(1) - Fe(1) - C(6) - C(7)	16.23(15)
C(3) - Fe(1) - C(6) - C(7)	175.28(11)
C(5) - Fe(1) - C(6) - C(7)	126.30(16)
C(4) - Fe(1) - C(6) - C(7)	93.20(12)
C(5) - C(6) - C(7) - C(8)	-45.1(2)
Fe(1) - C(6) - C(7) - C(8)	-102.11(15)
C(5) - C(6) - C(7) - Fe(1)	56.97(14)
C(2) - Fe(1) - C(7) - C(6)	91.70(12)
C(1) - Fe(1) - C(7) - C(6)	-168.76(11)
C(3) - Fe(1) - C(7) - C(6)	-14.3(3)
C(5) - Fe(1) - C(7) - C(6)	-33.39(12)
C(4) - Fe(1) - C(7) - C(6)	-74.45(12)
C(2) - Fe(1) - C(7) - C(8)	-153.69(12)
C(1) - Fe(1) - C(7) - C(8)	-54.15(13)
C(3) - Fe(1) - C(7) - C(8)	100.3(3)
C(6) - Fe(1) - C(7) - C(8)	114.61(17)
C(5) - Fe(1) - C(7) - C(8)	81.22(12)
C(4) - Fe(1) - C(7) - C(8)	40.16(11)
C(6) - C(7) - C(8) - O(4)	167.98(15)
Fe(1) - C(7) - C(8) - O(4)	91.80(14)
C(6) - C(7) - C(8) - C(10)	-76.92(19)
Fe(1) - C(7) - C(8) - C(10)	-153.10(11)
C(6) - C(7) - C(8) - C(9)	45.1(2)
Fe(1) - C(7) - C(8) - C(9)	-31.06(16)
C(5) - C(4) - C(9) - O(7)	-160.29(15)
Fe(1) - C(4) - C(9) - O(7)	-84.13(14)
C(5) - C(4) - C(9) - C(8)	-41.0(2)
Fe(1) - C(4) - C(9) - C(8)	35.21(16)
O(4) - C(8) - C(9) - O(7)	-4.99(19)
C(7) - C(8) - C(9) - O(7)	116.34(15)
C(10) - C(8) - C(9) - O(7)	-125.08(15)
O(4) - C(8) - C(9) - C(4)	-124.27(15)
C(7) - C(8) - C(9) - C(4)	-2.94(19)
C(10) - C(8) - C(9) - C(4)	115.64(15)
C(11) - O(6) - C(10) - O(5)	1.0(3)

C(11) - O(6) - C(10) - C(8)	-174.35(15)
O(4) - C(8) - C(10) - O(5)	21.8(2)
C(7) - C(8) - C(10) - O(5)	-94.8(2)
C(9) - C(8) - C(10) - O(5)	144.58(17)
O(4) - C(8) - C(10) - O(6)	-162.90(14)
C(7) - C(8) - C(10) - O(6)	80.55(17)
C(9) - C(8) - C(10) - O(6)	-40.10(19)

Symmetry transformations used to generate equivalent atoms:

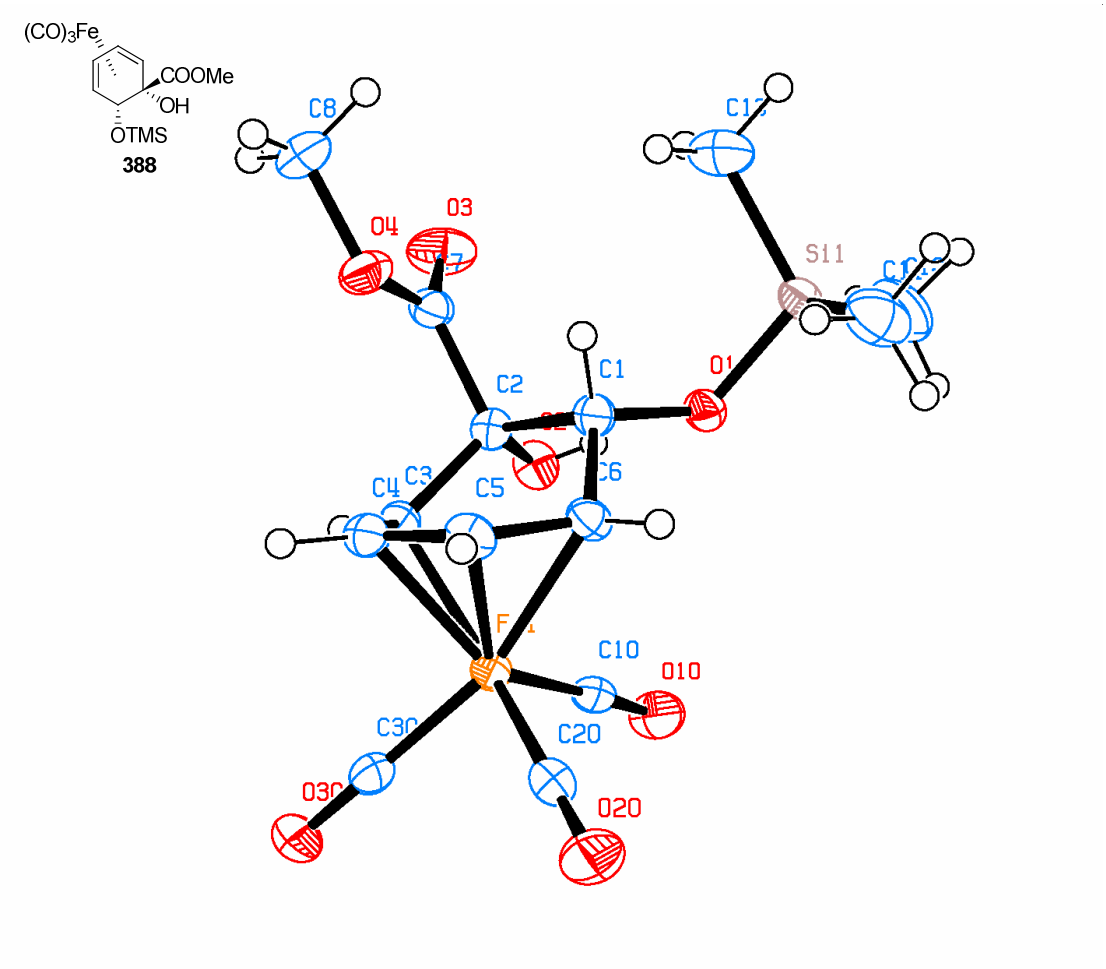


Figure 14 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **388**

Table 12 Crystal data and structure refinement for 388

Identification code	k10sel2
Empirical formula	C14 H18 Fe O7 Si
Formula weight	382.22
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, $P\ 2_1$

Unit cell dimensions	a = 11.7832(2) A $\alpha = 90^o$ b = 6.61340(10) A $\beta = 101.4370(10)^o$ c = 22.3223(5) A $\gamma = 90^o$
Volume	1704.97(5) $Å^3$
Z, Calculated density	4, 1.489 Mg/m^3
Absorption coefficient	0.985 mm^{-1}
F(000)	792
Crystal size	0.38 x 0.15 x 0.15 mm
Theta range for data collection	2.99 to 27.50^o
Limiting indices	-15<=h<=15, -8<=k<=8, -29<=l<=28
Reflections collected / unique	30516 / 7382 [R(int) = 0.0607]
Completeness to theta = 27.50	91.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7382 / 1 / 447
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0724
R indices (all data)	R1 = 0.0591, wR2 = 0.0804
Absolute structure parameter	-0.014(11)
Largest diff. peak and hole	0.340 and -0.442 $e.A^{-3}$

Table 13 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 388. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	2997(1)	10090(1)	9472(1)	21(1)
C(10)	3227(2)	7411(4)	9507(1)	26(1)
O(10)	3437(2)	5723(3	9531(1)	38(1)
C(20)	4295(3)	10827(5)	9232(1)	29(1)
O(20)	5125(2)	11352(4)	9076(1)	42(1)
C(30)	3600(2)	10706(4)	10255(2)	26(1)
O(30)	3979(2)	11088(4)	10754(1)	42(1)
O(1)	899(2)	6958(3)	8282(1)	24(1)
O(2)	696(2)	6746(3)	9410(1)	28(1)
O(3)	-1513(2)	8124(4)	9153(1)	43(1)
O(4)	-917(2)	11267(3)	8996(1)	34(1)
C(1)	862(2)	8933(4)	8538(1)	23(1)
C(2)	537(2)	8740(4)	9179(1)	22(1)
C(3)	1296(2)	10151(4)	9626(2)	21(1)
C(4)	1636(2)	12060(4)	9424(1)	24(1)
C(5)	2029(2)	12027(4)	8869(1)	25(1)
C(6)	1986(3)	10080(5)	8588(2)	24(1)
C(7)	-749(3)	9293(5)	9117(2)	26(1)
C(8)	-2103(3)	11974(6)	8920(2)	45(1)
Si(1)	152(1)	6477(1)	7578(1)	25(1)
C(11)	874(3)	7805(6)	7022(2)	47(1)
C(12)	163(4)	3730(5)	7498(2)	55(1)
C(13)	-1351(3)	7447(6)	7487(2)	51(1)
Fe(2)	2069(1)	452(1)	5531(1)	22(1)
C(40)	1757(2)	-2209(4)	5516(1)	26(1)
O(40)	1509(2)	-3873(3)	5497(1)	37(1)
C(50)	793(3)	1332(4)	5768(2)	31(1)
O(50)	-26(2)	1908(4)	5923(1)	45(1)
C(60)	1490(3)	1043(5)	4747(2)	31(1)
O(60)	1124(2)	1414(4)	4245(1)	48(1)
O(5)	3945(2)	-2674(3)	6769(1)	25(1)

O(6)	4208(2)	-3194(3)	5638(1)	27(1)
O(7)	6036(2)	1102(3)	5957(1)	33(1)
O(8)	6461(2)	-2217(4)	5952(1)	42(1)
C(21)	4135(2)	-819(4)	6488(1)	21(1)
C(22)	4455(2)	-1193(4)	5846(1)	22(1)
C(23)	3771(2)	226(4)	5383(2)	23(1)
C(24)	3510(2)	2221(4)	5543(1)	24(1)
C(25)	3117(2)	2402(4)	6098(1)	27(1)
C(26)	3086(3)	535(5)	6414(2)	24(1)
C(27)	5768(3)	-853(5)	5919(2)	25(1)
C(28)	7264(3)	1563(6)	6035(2)	46(1)
Si(2)	4793(1)	-3612(1)	7397(1)	27(1)
C(31)	3818(3)	-4901(5)	7831(2)	47(1)
C(32)	5624(3)	-1540(5)	7842(2)	41(1)
C(33)	5789(3)	-5491(5)	7161(2)	41(1)

Table 14 Bond lengths [Å] for 388

Fe(1) -C(20)	1.786(3)	C(13) -H(13A)	0.9800
Fe(1) -C(10)	1.791(3)	C(13) -H(13B)	0.9800
Fe(1) -C(30)	1.797(3)	C(13) -H(13C)	0.9800
Fe(1) -C(5)	2.036(3)	Fe(2) -C(50)	1.788(3)
Fe(1) -C(4)	2.053(3)	Fe(2) -C(60)	1.791(4)
Fe(1) -C(6)	2.094(3)	Fe(2) -C(40)	1.796(3)
Fe(1) -C(3)	2.100(3)	Fe(2) -C(25)	2.042(3)
C(10) -O(10)	1.142(3)	Fe(2) -C(24)	2.058(3)
C(20) -O(20)	1.156(4)	Fe(2) -C(26)	2.095(3)
C(30) -O(30)	1.143(4)	Fe(2) -C(23)	2.102(3)
O(1) -C(1)	1.430(3)	C(40) -O(40)	1.138(3)
O(1) -Si(1)	1.671(2)	C(50) -O(50)	1.152(4)
O(2) -C(2)	1.415(3)	C(60) -O(60)	1.144(4)
O(2) -H(2A)	0.73(4)	O(5) -C(21)	1.415(3)
O(3)- C(7)	1.201(4)	O(5) -Si(2)	1.671(2)
O(4) -C(7)	1.340(4)	O(6) -C(22)	1.414(3)
O(4) -C(8)	1.451(4)	O(6) -H(6A)	0.72(4)
C(1) -C(6)	1.511(4)	O(7) -C(27)	1.330(4)
C(1) -C(2)	1.558(4)	O(7) -C(28)	1.454(4)
C(1)- H(1)	1.0000	O(8) -C(27)	1.209(4)
C(2) -C(3)	1.521(4)	C(21)-C(26)	1.509(4)
C(2) -C(7)	1.538(4)	C(21) -C(22)	1.572(4)
C(3) -C(4)	1.424(4)	C(21) -H(21)	1.0000
C(3) -H(3)	0.90(3)	C(22) -C(23)	1.507(4)
C(4) -C(5)	1.407(4)	C(22) -C(27)	1.540(4)
C(4) -H(4)	0.9500	C(23) -C(24)	1.417(4)
C(5) -C(6)	1.429(4)	C(23) -H(23)	0.91(3)
C(5)- H(5)	0.9500	C(24) -C(25)	1.411(4)
C(6) -H(6)	0.90(3)	C(24) -H(24)	0.9500
C(8) -H(8A)	0.9800	C(25) -C(26)	1.426(4)
C(8) -H(8B)	0.9800	C(25) -H(25)	0.9500
C(8)- H(8C)	0.9800	C(26) -H(26)	0.95(3)
Si(1) -C(12)	1.825(4)	C(28) -H(28A)	0.9800
Si(1) -C(13)	1.857(4)	C(28) -H(28B)	0.9800
Si(1) -C(11)	1.859(4)	C(28) -H(28C)	0.9800
C(11) -H(11A)	0.9800	Si(2) -C(31)	1.851(3)
C(11) -H(11B)	0.9800	Si(2) -C(32)	1.854(3)
C(11) -H(11C)	0.9800	Si(2) -C(33)	1.856(3)
C(12) -H(12A)	0.9800	C(31) -H(31A)	0.9800
C(12) -H(12B)	0.9800	C(31) -H(31B)	0.9800
C(12) -H(12C)	0.9800	C(31) -H(31C)	0.9800
C(33) -H(33A)	0.9800	C(32) -H(32A)	0.9800
C(33) -H(33B)	0.9800	C(32) -H(32B)	0.9800
C(33) -H(33C)	0.9800	C(32) -H(32C)	0.9800

Table 15 Bond angles [deg] for 388

C(20)-Fe(1)-C(10)	98.73(13)	C(20)-Fe(1)-C(5)	91.76(13)
C(20)-Fe(1)-C(30)	91.86(13)	C(10)-Fe(1)-C(5)	135.29(13)
C(10)-Fe(1)-C(30)	98.91(14)	H(33B)-C(33)-H(33C)	109.5
C(30)-Fe(1)-C(5)	124.19(12)	Fe(1)-C(3)-H(3)	124(2)
C(20)-Fe(1)-C(4)	121.19(13)	C(5)-C(4)-C(3)	115.3(3)
C(10)-Fe(1)-C(4)	137.72(12)	C(5)-C(4)-Fe(1)	69.24(16)
C(30)-Fe(1)-C(4)	93.50(12)	C(3)-C(4)-Fe(1)	71.73(16)
C(5)-Fe(1)-C(4)	40.25(11)	C(5)-C(4)-H(4)	122.3
C(20)-Fe(1)-C(6)	94.53(13)	C(3)-C(4)-H(4)	122.3
C(10)-Fe(1)-C(6)	95.19(13)	Fe(1)-C(4)-H(4)	128.6
C(30)-Fe(1)-C(6)	163.45(13)	C(4)-C(5)-C(6)	114.3(3)
C(5)-Fe(1)-C(6)	40.45(12)	C(4)-C(5)-Fe(1)	70.51(16)
C(4)-Fe(1)-C(6)	70.15(12)	C(6)-C(5)-Fe(1)	71.94(17)
C(20)-Fe(1)-C(3)	161.05(13)	C(4)-C(5)-H(5)	122.8
C(10)-Fe(1)-C(3)	98.81(12)	C(6)-C(5)-H(5)	122.8
C(30)-Fe(1)-C(3)	92.44(13)	Fe(1)-C(5)-H(5)	126.4
C(5)-Fe(1)-C(3)	70.64(12)	C(5)-C(6)-C(1)	116.0(3)
C(4)-Fe(1)-C(3)	40.09(11)	C(5)-C(6)-Fe(1)	67.61(17)
C(6)-Fe(1)-C(3)	76.80(13)	C(1)-C(6)-Fe(1)	113.4(2)
O(10)-C(10)-Fe(1)	176.2(2)	C(5)-C(6)-H(6)	117(2)
O(20)-C(20)-Fe(1)	178.3(3)	C(1)-C(6)-H(6)	112(2)
O(30)-C(30)-Fe(1)	179.6(3)	Fe(1)-C(6)-H(6)	124(2)
C(1)-O(1)-Si(1)	119.82(17)	O(3)-C(7)-O(4)	123.9(3)
C(2)-O(2)-H(2A)	108(3)	O(3)-C(7)-C(2)	125.3(3)
C(7)-O(4)-C(8)	116.0(3)	O(4)-C(7)-C(2)	110.7(2)
O(1)-C(1)-C(6)	113.1(2)	O(4)-C(8)-H(8A)	109.5
O(1)-C(1)-C(2)	109.0(2)	O(4)-C(8)-H(8B)	109.5
C(6)-C(1)-C(2)	110.2(2)	H(8A)-C(8)-H(8B)	109.5
O(1)-C(1)-H(1)	108.2	O(4)-C(8)-H(8C)	109.5
C(6)-C(1)-H(1)	108.2	H(8A)-C(8)-H(8C)	109.5
C(2)-C(1)-H(1)	108.2	H(8B)-C(8)-H(8C)	109.5
O(2)-C(2)-C(3)	108.3(2)	O(1)-Si(1)-C(12)	105.61(15)
O(2)-C(2)-C(7)	108.1(2)	O(1)-Si(1)-C(13)	110.49(15)
C(3)-C(2)-C(7)	110.7(2)	C(12)-Si(1)-C(13)	111.0(2)
O(2)-C(2)-C(1)	111.9(2)	O(1)-Si(1)-C(11)	108.18(14)
C(3)-C(2)-C(1)	109.5(2)	C(12)-Si(1)-C(11)	113.1(2)
C(7)-C(2)-C(1)	108.3(2)	C(13)-Si(1)-C(11)	108.44(19)
C(4)-C(3)-C(2)	120.1(3)	Si(1)-C(11)-H(11A)	109.5
C(4)-C(3)-Fe(1)	68.17(17)	Si(1)-C(11)-H(11B)	109.5
C(2)-C(3)-Fe(1)	109.7(2)	H(11A)-C(11)-H(11B)	109.5
C(4)-C(3)-H(3)	119(2)	Si(1)-C(11)-H(11C)	109.5
C(2)-C(3)-H(3)	111(2)	H(11A)-C(11)-H(11C)	109.5
C(40)-Fe(2)-C(24)	136.27(12)	H(11B)-C(11)-H(11C)	109.5
C(25)-Fe(2)-C(24)	40.24(12)	Si(1)-C(12)-H(12A)	109.5
C(50)-Fe(2)-C(26)	94.05(13)	Si(1)-C(12)-H(12B)	109.5
C(60)-Fe(2)-C(26)	161.78(13)	H(12A)-C(12)-H(12B)	109.5
C(40)-Fe(2)-C(26)	96.86(13)	Si(1)-C(12)-H(12C)	109.5
C(25)-Fe(2)-C(26)	40.32(12)	H(12A)-C(12)-H(12C)	109.5
C(24)-Fe(2)-C(26)	69.89(12)	H(12B)-C(12)-H(12C)	109.5
C(50)-Fe(2)-C(23)	162.67(13)	Si(1)-C(13)-H(13A)	109.5
C(60)-Fe(2)-C(23)	93.00(13)	Si(1)-C(13)-H(13B)	109.5
C(40)-Fe(2)-C(23)	97.24(12)	H(13A)-C(13)-H(13B)	109.5
C(25)-Fe(2)-C(23)	70.34(12)	Si(1)-C(13)-H(13C)	109.5
C(24)-Fe(2)-C(23)	39.81(11)	H(13A)-C(13)-H(13C)	109.5
C(26)-Fe(2)-C(23)	76.36(13)	H(13B)-C(13)-H(13C)	109.5
O(40)-C(40)-Fe(2)	177.0(3)	C(50)-Fe(2)-C(60)	92.20(14)
O(50)-C(50)-Fe(2)	179.6(3)	C(50)-Fe(2)-C(40)	98.23(13)
O(60)-C(60)-Fe(2)	179.7(3)	C(60)-Fe(2)-C(40)	99.16(14)
C(21)-O(5)-Si(2)	124.97(17)	C(50)-Fe(2)-C(25)	92.95(13)
C(22)-O(6)-H(6A)	110(4)	C(60)-Fe(2)-C(25)	122.28(13)
C(27)-O(7)-C(28)	115.5(3)	C(40)-Fe(2)-C(25)	136.57(12)
O(5)-C(21)-C(26)	111.4(2)	C(50)-Fe(2)-C(24)	123.44(13)
O(5)-C(21)-C(22)	110.8(2)	C(60)-Fe(2)-C(24)	92.42(13)
C(26)-C(21)-C(22)	109.4(2)	O(5)-C(21)-H(21)	108.4
C(26)-C(21)-H(21)	108.4	C(22)-C(21)-H(21)	108.4
O(6)-C(22)-C(23)	108.1(2)	O(6)-C(22)-C(27)	108.0(2)
C(23)-C(22)-C(27)	111.8(2)	O(6)-C(22)-C(21)	112.1(2)
C(23)-C(22)-C(21)	109.6(2)	C(27)-C(22)-C(21)	107.4(2)
C(24)-C(23)-C(22)	121.3(3)	C(24)-C(23)-Fe(2)	68.44(17)
C(22)-C(23)-Fe(2)	109.5(2)	C(24)-C(23)-H(23)	118.2(17)

C(22)-C(23)-H(23)	112.8(17)	Fe(2)-C(23)-H(23)	119.2(16)
C(25)-C(24)-C(23)	115.2(3)	C(25)-C(24)-Fe(2)	69.26(16)
C(23)-C(24)-Fe(2)	71.75(16)	C(25)-C(24)-H(24)	122.4
C(23)-C(24)-H(24)	122.4	Fe(2)-C(24)-H(24)	128.5
C(24)-C(25)-C(26)	114.0(3)	C(24)-C(25)-Fe(2)	70.50(17)
C(26)-C(25)-Fe(2)	71.83(17)	C(24)-C(25)-H(25)	123.0
C(26)-C(25)-H(25)	123.0	Fe(2)-C(25)-H(25)	126.3
C(25)-C(26)-C(21)	117.9(3)	C(25)-C(26)-Fe(2)	67.86(18)
C(21)-C(26)-Fe(2)	113.1(2)	C(25)-C(26)-H(26)	115.9(17)
C(21)-C(26)-H(26)	117.1(18)	Fe(2)-C(26)-H(26)	115.7(17)
O(8)-C(27)-O(7)	124.9(3)	O(8)-C(27)-C(22)	123.4(3)
O(7)-C(27)-C(22)	111.7(2)	O(7)-C(28)-H(28A)	109.5
O(7)-C(28)-H(28B)	109.5	H(28A)-C(28)-H(28B)	109.5
O(7)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	O(5)-Si(2)-C(31)	106.28(14)
O(5)-Si(2)-C(32)	109.79(13)	C(31)-Si(2)-C(32)	112.14(18)
O(5)-Si(2)-C(33)	108.51(14)	C(31)-Si(2)-C(33)	109.49(17)
C(32)-Si(2)-C(33)	110.48(16)	Si(2)-C(31)-H(31A)	109.5
Si(2)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
Si(2)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	Si(2)-C(32)-H(32A)	109.5
Si(2)-C(32)-H(32B)	109.5	H(32A)-C(32)-H(32B)	109.5
Si(2)-C(32)-H(32C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5	Si(2)-C(33)-H(33A)	109.5
Si(2)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
Si(2)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5

Table 16 Anisotropic displacement parameters (A^2 x 10^3) for 388. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	19(1)	21(1)	23(1)	-2(1)	4(1)	-2(1)
C(10)	18(2)	28(2)	29(2)	-5(1)	1(1)	-3(1)
O(10)	32(1)	23(1)	56(2)	-4(1)	1(1)	0(1)
C(20)	29(2)	29(2)	27(2)	-6(1)	3(1)	-3(1)
O(20)	29(1)	52(2)	49(2)	-1(1)	15(1)	-9(1)
C(30)	19(1)	30(2)	31(2)	-4(1)	7(1)	0(1)
O(30)	34(1)	61(2)	28(1)	-15(1)	-2(1)	3(1)
O(1)	24(1)	22(1)	26(1)	-3(1)	2(1)	-1(1)
O(2)	35(1)	22(1)	26(1)	3(1)	6(1)	-2(1)
O(3)	25(1)	55(2)	48(2)	13(1)	7(1)	-11(1)
O(4)	20(1)	37(1)	45(2)	-4(1)	5(1)	3(1)
C(1)	24(2)	19(1)	25(2)	0(1)	4(1)	0(1)
C(2)	23(2)	20(1)	22(2)	2(1)	5(1)	0(1)
C(3)	23(2)	24(2)	18(2)	1(1)	4(1)	2(1)
C(4)	24(2)	19(1)	29(2)	1(1)	2(1)	1(1)
C(5)	27(2)	20(1)	26(2)	3(1)	2(1)	-5(1)
C(6)	23(2)	29(2)	19(2)	-1(1)	4(1)	-4(1)
C(7)	22(2)	35(2)	21(2)	-1(1)	3(1)	1(1)
C(8)	27(2)	59(2)	48(2)	-9(2)	5(2)	17(2)
Si(1)	25(1)	28(1)	23(1)	-2(1)	2(1)	-4(1)
C(11)	42(2)	62(2)	34(2)	5(2)	4(2)	-11(2)
C(12)	72(3)	33(2)	50(3)	-6(2)	-9(2)	-5(2)
C(13)	29(2)	68(3)	51(2)	-4(2)	-3(2)	2(2)
Fe(2)	20(1)	20(1)	25(1)	2(1)	2(1)	1(1)
C(40)	19(2)	30(2)	26(2)	2(1)	2(1)	1(1)
O(40)	30(1)	24(1)	56(2)	3(1)	3(1)	-4(1)
C(50)	31(2)	27(2)	33(2)	5(1)	2(2)	-1(1)
O(50)	32(1)	53(2)	54(2)	-2(1)	13(1)	13(1)
C(60)	22(2)	30(2)	42(2)	7(1)	6(2)	-1(1)
O(60)	34(1)	71(2)	35(2)	21(1)	-5(1)	-8(1)
O(5)	26(1)	21(1)	28(1)	7(1)	3(1)	-4(1)
O(6)	30(1)	21(1)	28(1)	-2(1)	3(1)	1(1)
O(7)	22(1)	36(1)	41(2)	4(1)	6(1)	-8(1)
O(8)	26(1)	46(1)	51(2)	-9(1)	7(1)	10(1)

C(21)	22(2)	17(1)	22(2)	2(1)	2(1)	-1(1)
C(22)	19(2)	21(1)	24(2)	-1(1)	3(1)	-2(1)
C(23)	21(2)	26(2)	21(2)	0(1)	6(1)	-3(1)
C(24)	26(2)	20(1)	24(2)	3(1)	0(1)	-4(1)
C(25)	0(1)	-1(1)	-1(1)	28(2)	21(1)	28(2)
C(26)	24(2)	25(2)	22(2)	-2(1)	7(1)	2(1)
C(27)	28(2)	29(2)	20(2)	2(1)	6(1)	0(1)
C(28)	27(2)	61(2)	48(2)	7(2)	5(2)	-18(2)
Si(2)	27(1)	26(1)	25(1)	5(1)	2(1)	0(1)
C(31)	47(2)	48(2)	46(2)	20(2)	12(2)	3(2)
C(32)	50(2)	40(2)	29(2)	3(1)	-2(2)	-3(2)
C(33)	27(2)	36(2)	57(2)	-2(2)	1(2)	7(1)

Table 17 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 388

Atom	x	y	z	U(eq)
H(2A)	600(30)	6060(60)	9151(17)	38(12)
H(1)	238	9721	8267	27
H(3)	1120(30)	10060(50)	10001(16)	28(9)
H(4)	1599	13271	9649	29
H(5)	2300	13200	8695	30
H(6)	2270(30)	9980(50)	8246(15)	26(9)
H(8A)	-67	8574	11271	2585
H(8B)	-2129	13432	8841	67
H(8C)	-2396	11695	9293	67
H(11A)	915	9256	7114	70
H(11B)	429	7593	6607	70
H(11C)	1659	7269	7052	70
H(12A)	965	3247	7572	82
H(12B)	-228	3355	7084	82
H(12C)	-242	3115	7795	82
H(13A)	-1747	6750	7774	76
H(13B)	-1767	7201	7068	76
H(13C)	-1332	8903	7571	76
H(6A)	4480(40)	-3900(70)	5870(20)	61(15)
H(21)	4799	-112	6755	25
H(23)	3890(20)	0(40)	4998(13)	10(7)
H(24)	3594	3357	5295	29
H(25)	2893	3654	6247	32
H(26)	2670(20)	550(40)	6738(13)	15(7)
H(28A)	7679	969	6418	69
H(28B)	7373	3032	6046	69
H(28C)	69	5692	997	7566
H(31A)	3253	-3929	7928	71
H(31B)	4275	-5451	8211	71
H(31C)	3411	-6003	7585	71
H(32A)	6148	-934	7602	62
H(32B)	6075	-2083	8224	62
H(32C)	5087	-508	7934	62
H(33A)	5338	-6533	6907	62
H(33B)	6258	-6121	7525	62
H(33C)	6299	-4811	6927	62

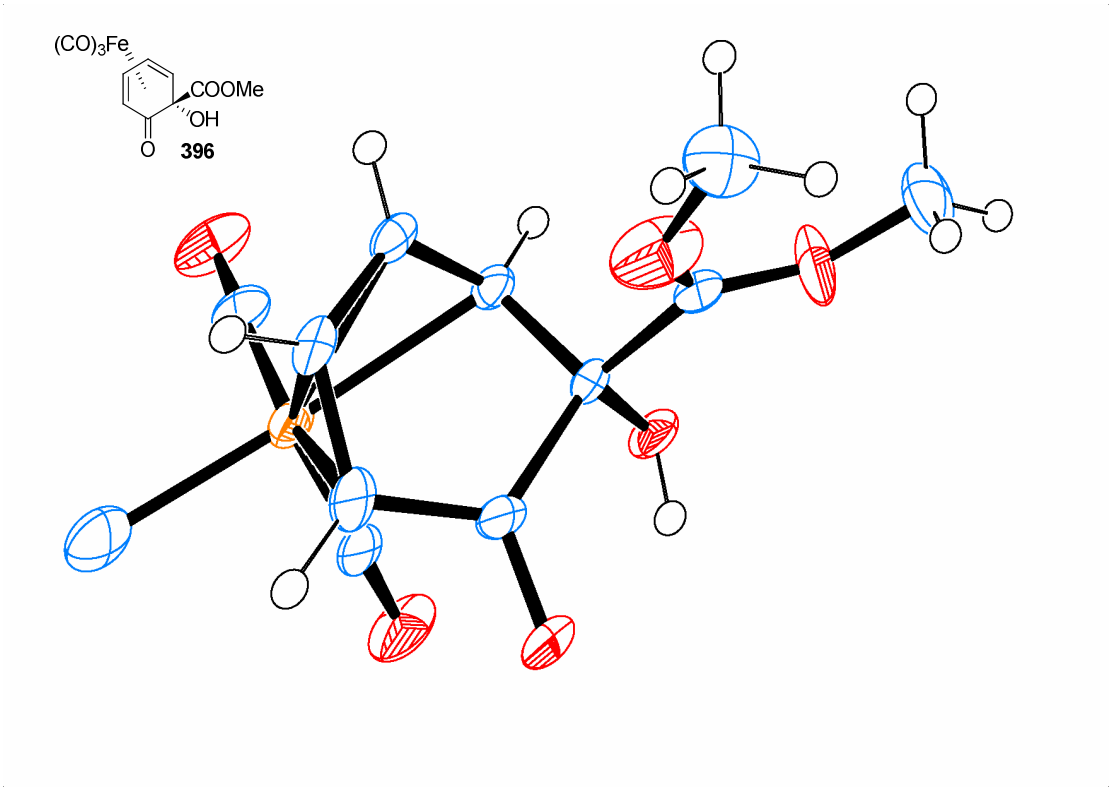


Figure 15

ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **396**

Table 18 Crystal data and structure refinement for 396

Identification code	k09sel1
Empirical formula	C11 H8 Fe O7
Formula weight	308.02
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 6.6880(3)Å α = 85.896(1)°
	b = 6.7010(3)Å β = 85.972(2)°
	c = 46.634(2)Å γ = 60.254(3)°
Volume	1808.47(15) Å^3
Z	6
Density (calculated)	1.697 Mg/m^3
Absorption coefficient	1.277 mm^{-1}
F(000)	936
Crystal size	0.22 x 0.07 x 0.07 mm
Theta range for data collection	4.21 to 25.00°
Index ranges	-7<=h<=7; -7<=k<=7; -55<=l<=55
Reflections collected	14425
Independent reflections	9757 [R(int) = 0.0357]
Reflections observed (>2σ)	8640

Data Completeness	0.937
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.787 and 0.745
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9757 / 27 / 1177
Goodness-of-fit on F^2	1.023
Final R indices [I>2σ(I)]	R1 = 0.0318 wR2 = 0.0629
R indices (all data)	R1 = 0.0418 wR2 = 0.0662
Absolute structure parameter	-0.017(10)
Largest diff. peak and hole	0.330 and -0.362 eÅ^{-3}

Notes:

…inserted directly into SEL manuscript – October '09, and added to CIF file…

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O4-H41	0.840	2.268	113.72	2.717	O5
O4A-H42	0.840	2.289	110.89	2.705	O5A
O4B-H43	0.840	2.305	110.53	2.716	O5B
O4C-H44	0.840	2.290	112.24	2.721	O5C
O4D-H45	0.840	2.264	113.32	2.709	O5D
O5E-H46	0.840	2.262	113.21	2.706	O6E

Table 19 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 396. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	11161(1)	3236(1)	4(1)	19(1)
Fe(1A)	10429(1)	-1003(1)	2191(1)	19(1)
Fe(1B)	4017(1)	1988(1)	3338(1)	19(1)
Fe(1C)	-175(1)	4734(1)	5523(1)	19(1)
Fe(1D)	6066(1)	10376(1)	6669(1)	19(1)
Fe(1E)	8903(1)	9635(1)	8858(1)	20(1)
O(1)	7871(6)	6954(6)	-376(1)	37(1)
O(2)	11345(7)	-627(7)	-281(1)	41(1)
O(3)	15506(6)	2620(7)	-280(1)	41(1)
O(4)	5309(5)	7198(5)	224(1)	25(1)
O(5)	8010(5)	9055(5)	311(1)	27(1)
O(6)	4351(7)	6895(7)	777(1)	64(1)
O(7)	8044(7)	5301(7)	892(1)	52(1)
O(1A)	6809(6)	-1203(7)	2571(1)	38(1)
O(2A)	10702(7)	2666(7)	2469(1)	36(1)
O(3A)	14454(7)	-4726(7)	2481(1)	48(1)
O(4A)	4717(5)	817(5)	1968(1)	25(1)
O(5A)	7435(5)	-3735(5)	1887(1)	27(1)
O(6A)	4145(7)	1902(7)	1412(1)	66(1)
O(7A)	7906(8)	-252(7)	1299(1)	52(1)
O(1B)	7744(6)	1954(7)	2957(1)	37(1)
O(2B)	145(7)	5937(7)	3052(1)	40(1)
O(3B)	3379(7)	-1456(7)	3054(1)	39(1)
O(4B)	8002(5)	3652(5)	3559(1)	25(1)
O(5B)	9848(5)	-970(5)	3644(1)	26(1)

O(6B)	7685(7)	4386(7)	4111(1)	63(1)
O(7B)	6105(7)	2136(7)	4227(1)	51(1)
O(1C)	-465(6)	8199(6)	5905(1)	38(1)
O(2C)	3590(7)	667(7)	5809(1)	41(1)
O(3C)	-3810(7)	3899(7)	5806(1)	41(1)
O(4C)	1639(5)	8864(5)	5302(1)	23(1)
O(5C)	-2943(5)	10762(5)	5216(1)	25(1)
O(6C)	2709(7)	8941(7)	4748(1)	61(1)
O(7C)	564(7)	7414(7)	4633(1)	52(1)
O(1D)	6151(7)	6996(6)	6289(1)	40(1)
O(2D)	9931(7)	10826(7)	6392(1)	39(1)
O(3D)	2514(7)	14598(7)	6380(1)	48(1)
O(4D)	7744(5)	4522(5)	6893(1)	25(1)
O(5D)	3126(5)	7192(5)	6975(1)	27(1)
O(6D)	8458(7)	3577(7)	7447(1)	67(1)
O(7D)	6230(7)	7291(8)	7559(1)	52(1)
O(2E)	12326(6)	6013(6)	9239(1)	37(1)
O(3E)	4692(6)	9883(7)	9134(1)	38(1)
O(4E)	8336(8)	13664(7)	9148(1)	49(1)
O(5E)	12983(5)	3945(5)	8632(1)	25(1)
O(6E)	14895(5)	6688(5)	8552(1)	27(1)
O(7E)	13017(7)	3384(7)	8080(1)	69(1)
O(8E)	11513(6)	7153(8)	7966(1)	55(1)
C(1)	9134(9)	5500(9)	-234(1)	26(1)
C(2)	11314(8)	844(9)	-171(1)	28(1)
C(3)	13836(8)	2826(8)	-171(1)	26(1)
C(4)	8548(8)	3472(8)	306(1)	18(1)
C(5)	10768(7)	2005(7)	410(1)	20(1)
C(6)	12218(8)	2948(8)	417(1)	22(1)
C(7)	11311(7)	5299(8)	320(1)	19(1)
C(8)	8858(7)	6967(8)	348(1)	18(1)
C(9)	7255(7)	5939(7)	400(1)	18(1)
C(10)	6483(8)	6060(7)	715(1)	22(1)
C(11)	3157(18)	7250(20)	1041(2)	42(3)
C(12)	8130(20)	4930(20)	1192(2)	46(3)
C(1A)	8200(9)	-1093(9)	2427(1)	25(1)
C(2A)	10595(8)	1249(9)	2363(1)	25(1)
C(3A)	12931(9)	-3276(9)	2368(1)	31(1)
C(4A)	8012(8)	1274(8)	1889(1)	16(1)
C(5A)	10322(7)	494(8)	1787(1)	20(1)
C(6A)	11780(8)	-1897(8)	1779(1)	22(1)
C(7A)	10758(8)	-3296(8)	1873(1)	20(1)
C(8A)	8347(7)	-2537(7)	1848(1)	17(1)
C(9A)	6774(7)	76(7)	1796(1)	19(1)
C(10A)	6233(8)	615(8)	1474(1)	24(1)
C(11A)	3165(19)	2610(20)	1155(2)	47(3)
C(12A)	8180(20)	-74(19)	1007(2)	40(3)
C(1B)	6298(9)	1968(9)	3098(1)	24(1)
C(2B)	1621(8)	4412(9)	3159(1)	27(1)
C(3B)	3611(8)	-104(9)	3162(1)	29(1)
C(4B)	4279(8)	4050(8)	3639(1)	19(1)
C(5B)	2775(7)	3231(8)	3743(1)	19(1)
C(6B)	3710(8)	813(8)	3751(1)	22(1)
C(7B)	6086(8)	-537(8)	3654(1)	20(1)
C(8B)	7744(8)	237(8)	3682(1)	22(1)
C(9B)	6746(7)	2805(7)	3731(1)	18(1)
C(10B)	6864(7)	3152(8)	4050(1)	24(1)
C(11B)	8050(20)	4930(20)	4374(2)	42(3)
C(12B)	5790(20)	2120(20)	4527(2)	47(3)
C(1C)	-332(9)	6855(9)	5760(1)	24(1)
C(2C)	2127(9)	2221(9)	5698(1)	29(1)
C(3C)	-2382(9)	4203(8)	5698(1)	29(1)
C(4C)	2095(7)	5193(8)	5222(1)	18(1)
C(5C)	1334(8)	3760(8)	5118(1)	21(1)
C(6C)	-1094(8)	4704(8)	5109(1)	23(1)
C(7C)	-2509(8)	7021(8)	5206(1)	21(1)
C(8C)	-1712(7)	8667(8)	5180(1)	19(1)
C(9C)	912(7)	7718(7)	5128(1)	18(1)
C(10C)	1445(7)	8043(7)	4810(1)	23(1)
C(11C)	3430(20)	9460(20)	4486(2)	45(3)
C(12C)	770(20)	7270(20)	4337(2)	48(3)

C(1D)	6124(9)	8302(9)	6430(1)	25(1)
C(2D)	8448(9)	10643(8)	6498(1)	25(1)
C(3D)	3888(9)	12992(9)	6492(1)	30(1)
C(4D)	8148(8)	7769(8)	6971(1)	18(1)
C(5D)	7297(8)	10008(8)	7073(1)	20(1)
C(6D)	4906(8)	11443(9)	7082(1)	22(1)
C(7D)	3568(8)	10487(8)	6985(1)	19(1)
C(8D)	4305(7)	8067(8)	7014(1)	17(1)
C(9D)	6904(7)	6446(7)	7066(1)	17(1)
C(10D)	7240(7)	5693(8)	7385(1)	23(1)
C(11D)	9030(20)	2434(18)	7705(2)	48(3)
C(12D)	6244(18)	7360(20)	7854(2)	39(3)
C(1E)	10990(9)	7401(9)	9095(1)	24(1)
C(2E)	6334(9)	9795(8)	9027(1)	28(1)
C(3E)	8523(8)	12132(9)	9036(1)	31(1)
C(4E)	9326(7)	7239(8)	8556(1)	18(1)
C(5E)	7910(8)	9538(8)	8450(1)	20(1)
C(6E)	8870(8)	11000(8)	8445(1)	21(1)
C(7E)	11177(8)	9985(8)	8541(1)	22(1)
C(8E)	12830(7)	7564(7)	8514(1)	18(1)
C(9E)	11851(7)	5997(7)	8462(1)	19(1)
C(10E)	12151(7)	5460(8)	8140(1)	25(1)
C(11E)	13580(20)	2381(19)	7825(2)	46(3)
C(12E)	11380(20)	7430(20)	7664(2)	44(3)

Table 20 Bond lengths [Å] and angles [^{o}] for 396.

Fe(1)-C(2)	1.805(6)	Fe(1)-C(3)	1.811(5)
Fe(1)-C(1)	1.816(5)	Fe(1)-C(6)	2.058(4)
Fe(1)-C(5)	2.064(4)	Fe(1)-C(4)	2.114(5)
Fe(1)-C(7)	2.132(4)	Fe(1A)-C(2A)	1.811(5)
Fe(1A)-C(3A)	1.812(5)	Fe(1A)-C(1A)	1.813(6)
Fe(1A)-C(5A)	2.060(4)	Fe(1A)-C(6A)	2.062(5)
Fe(1A)-C(4A)	2.121(5)	Fe(1A)-C(7A)	2.133(5)
Fe(1B)-C(3B)	1.813(6)	Fe(1B)-C(2B)	1.820(5)
Fe(1B)-C(1B)	1.822(6)	Fe(1B)-C(6B)	2.066(5)
Fe(1B)-C(5B)	2.067(4)	Fe(1B)-C(4B)	2.114(5)
Fe(1B)-C(7B)	2.135(5)	Fe(1C)-C(2C)	1.810(5)
Fe(1C)-C(3C)	1.811(6)	Fe(1C)-C(1C)	1.818(6)
Fe(1C)-C(5C)	2.068(5)	Fe(1C)-C(6C)	2.074(4)
Fe(1C)-C(4C)	2.115(5)	Fe(1C)-C(7C)	2.145(4)
Fe(1D)-C(2D)	1.814(6)	Fe(1D)-C(3D)	1.819(5)
Fe(1D)-C(1D)	1.827(6)	Fe(1D)-C(5D)	2.059(4)
Fe(1D)-C(6D)	2.064(5)	Fe(1D)-C(4D)	2.117(5)
Fe(1D)-C(7D)	2.123(5)	Fe(1E)-C(2E)	1.796(6)
Fe(1E)-C(3E)	1.817(6)	Fe(1E)-C(1E)	1.823(5)
Fe(1E)-C(6E)	2.066(5)	Fe(1E)-C(5E)	2.072(4)
Fe(1E)-C(4E)	2.111(5)	Fe(1E)-C(7E)	2.130(5)
O(1)-C(1)	1.128(6)	O(2)-C(2)	1.134(6)
O(3)-C(3)	1.142(6)	O(4)-C(9)	1.428(5)
O(4)-H(41)	0.8400	O(5)-C(8)	1.226(5)
O(6)-C(10)	1.266(5)	O(6)-C(11)	1.387(10)
O(7)-C(10)	1.250(5)	O(7)-C(12)	1.404(10)
O(1A)-C(1A)	1.137(6)	O(2A)-C(2A)	1.138(6)
O(3A)-C(3A)	1.130(6)	O(4A)-C(9A)	1.416(5)
O(4A)-H(42)	0.8400	O(5A)-C(8A)	1.225(5)
O(6A)-C(10A)	1.265(5)	O(6A)-C(11A)	1.348(10)
O(7A)-C(10A)	1.243(6)	O(7A)-C(12A)	1.366(9)
O(1B)-C(1B)	1.126(6)	O(2B)-C(2B)	1.124(6)
O(3B)-C(3B)	1.145(6)	O(4B)-C(9B)	1.410(5)
O(4B)-H(43)	0.8400	O(5B)-C(8B)	1.234(5)
O(6B)-C(10B)	1.254(5)	O(6B)-C(11B)	1.378(9)
O(7B)-C(10B)	1.268(6)	O(7B)-C(12B)	1.403(10)
O(1C)-C(1C)	1.131(6)	O(2C)-C(2C)	1.138(6)
O(3C)-C(3C)	1.147(6)	O(4C)-C(9C)	1.416(5)
O(4C)-H(44)	0.8400	O(5C)-C(8C)	1.242(5)
O(6C)-C(10C)	1.267(5)	O(6C)-C(11C)	1.368(10)
O(7C)-C(10C)	1.253(5)	O(7C)-C(12C)	1.385(10)

O(1D)-C(1D)	1.126(6)	O(2D)-C(2D)	1.134(6)
O(3D)-C(3D)	1.131(6)	O(4D)-C(9D)	1.415(5)
O(4D)-H(45)	0.8400	O(5D)-C(8D)	1.222(5)
O(6D)-C(10D)	1.259(5)	O(6D)-C(11D)	1.353(10)
O(7D)-C(10D)	1.261(6)	O(7D)-C(12D)	1.383(10)
O(2E)-C(1E)	1.132(6)	O(3E)-C(2E)	1.149(6)
O(4E)-C(3E)	1.134(6)	O(5E)-C(9E)	1.411(5)
O(5E)-H(46)	0.8400	O(6E)-C(8E)	1.224(5)
O(7E)-C(10E)	1.258(5)	O(7E)-C(11E)	1.346(11)
O(8E)-C(10E)	1.250(6)	O(8E)-C(12E)	1.412(10)
C(4)-C(5)	1.412(6)	C(4)-C(9)	1.519(6)
C(4)-H(4)	0.979(5)	C(5)-C(6)	1.398(6)
C(5)-H(5)	0.979(5)	C(6)-C(7)	1.428(6)
C(6)-H(6)	0.980(5)	C(7)-C(8)	1.459(6)
C(7)-H(7)	0.980(5)	C(8)-C(9)	1.535(6)
C(9)-C(10)	1.519(6)	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(4A)-C(5A)	1.420(6)
C(4A)-C(9A)	1.508(6)	C(4A)-H(4A)	0.979(5)
C(5A)-C(6A)	1.404(6)	C(5A)-H(5A)	0.979(5)
C(6A)-C(7A)	1.440(6)	C(6A)-H(6A)	0.980(5)
C(7A)-C(8A)	1.441(6)	C(7A)-H(7A)	0.980(5)
C(8A)-C(9A)	1.542(6)	C(9A)-C(10A)	1.547(6)
C(11A)-H(11D)	0.9800	C(11A)-H(11E)	0.9800
C(11A)-H(11F)	0.9800	C(12A)-H(12D)	0.9800
C(12A)-H(12E)	0.9800	C(12A)-H(12F)	0.9800
C(4B)-C(5B)	1.410(6)	C(4B)-C(9B)	1.512(6)
C(4B)-H(4B)	0.980(5)	C(5B)-C(6B)	1.417(6)
C(5B)-H(5B)	0.979(5)	C(6B)-C(7B)	1.442(6)
C(6B)-H(6B)	0.979(5)	C(7B)-C(8B)	1.455(6)
C(7B)-H(7B)	0.979(5)	C(8B)-C(9B)	1.534(6)
C(9B)-C(10B)	1.532(6)	C(11B)-H(11G)	0.9800
C(11B)-H(11H)	0.9800	C(11B)-H(11I)	0.9800
C(12B)-H(12G)	0.9800	C(12B)-H(12H)	0.9800
C(12B)-H(12I)	0.9800	C(4C)-C(5C)	1.416(6)
C(4C)-C(9C)	1.515(6)	C(4C)-H(4C)	0.980(3)
C(5C)-C(6C)	1.423(6)	C(5C)-H(5C)	0.980(3)
C(6C)-C(7C)	1.448(7)	C(6C)-H(6C)	0.980(3)
C(7C)-C(8C)	1.439(6)	C(7C)-H(7C)	0.980(3)
C(8C)-C(9C)	1.548(6)	C(9C)-C(10C)	1.526(6)
C(11C)-H(11J)	0.9800	C(11C)-H(11K)	0.9800
C(11C)-H(11L)	0.9800	C(12C)-H(12J)	0.9800
C(12C)-H(12K)	0.9800	C(12C)-H(12L)	0.9800
C(4D)-C(5D)	1.421(6)	C(4D)-C(9D)	1.516(6)
C(4D)-H(4D)	0.91(6)	C(5D)-C(6D)	1.398(6)
C(5D)-H(5D)	0.93(6)	C(6D)-C(7D)	1.444(6)
C(6D)-H(6D)	0.97(6)	C(7D)-C(8D)	1.441(6)
C(7D)-H(7D)	0.95(7)	C(8D)-C(9D)	1.552(6)
C(9D)-C(10D)	1.529(6)	C(11D)-H(11M)	0.9800
C(11D)-H(11N)	0.9800	C(11D)-H(11O)	0.9800
C(12D)-H(12M)	0.9800	C(12D)-H(12N)	0.9800
C(12D)-H(12O)	0.9800	C(4E)-C(5E)	1.422(6)
C(4E)-C(9E)	1.513(6)	C(4E)-H(4E)	0.98(7)
C(5E)-C(6E)	1.411(6)	C(5E)-H(5E)	0.93(6)
C(6E)-C(7E)	1.434(6)	C(6E)-H(6E)	0.98(6)
C(7E)-C(8E)	1.449(6)	C(7E)-H(7E)	0.89(7)
C(8E)-C(9E)	1.526(6)	C(9E)-C(10E)	1.546(6)
C(11E)-H(11P)	0.9800	C(11E)-H(11Q)	0.9800
C(11E)-H(11R)	0.9800	C(12E)-H(12P)	0.9800
C(12E)-H(12Q)	0.9800	C(12E)-H(12R)	0.9800
C(2)-Fe(1)-C(3)	92.6(2)	C(2)-Fe(1)-C(1)	97.1(2)
C(3)-Fe(1)-C(1)	99.4(2)	C(2)-Fe(1)-C(6)	122.5(2)
C(3)-Fe(1)-C(6)	95.3(2)	C(1)-Fe(1)-C(6)	137.0(2)
C(2)-Fe(1)-C(5)	93.4(2)	C(3)-Fe(1)-C(5)	126.45(19)
C(1)-Fe(1)-C(5)	132.4(2)	C(6)-Fe(1)-C(5)	39.66(17)
C(2)-Fe(1)-C(4)	93.6(2)	C(3)-Fe(1)-C(4)	165.00(19)
C(1)-Fe(1)-C(4)	93.4(2)	C(6)-Fe(1)-C(4)	69.88(18)
C(5)-Fe(1)-C(4)	39.49(17)	C(2)-Fe(1)-C(7)	162.1(2)

C(3)-Fe(1)-C(7)	91.78(19)	C(1)-Fe(1)-C(7)	99.3(2)
C(6)-Fe(1)-C(7)	39.82(17)	C(5)-Fe(1)-C(7)	70.21(18)
C(4)-Fe(1)-C(7)	78.36(17)	C(2A)-Fe(1A)-C(3A)	93.2(2)
C(2A)-Fe(1A)-C(1A)	98.0(2)	C(3A)-Fe(1A)-C(1A)	98.7(2)
C(2A)-Fe(1A)-C(5A)	92.5(2)	C(3A)-Fe(1A)-C(5A)	127.6(2)
C(1A)-Fe(1A)-C(5A)	131.8(2)	C(2A)-Fe(1A)-C(6A)	120.6(2)
C(3A)-Fe(1A)-C(6A)	95.2(2)	C(1A)-Fe(1A)-C(6A)	138.0(2)
C(5A)-Fe(1A)-C(6A)	39.83(17)	C(2A)-Fe(1A)-C(4A)	94.44(19)
C(3A)-Fe(1A)-C(4A)	165.4(2)	C(1A)-Fe(1A)-C(4A)	92.5(2)
C(5A)-Fe(1A)-C(4A)	39.68(17)	C(6A)-Fe(1A)-C(4A)	70.21(18)
C(2A)-Fe(1A)-C(7A)	160.7(2)	C(3A)-Fe(1A)-C(7A)	90.7(2)
C(1A)-Fe(1A)-C(7A)	100.1(2)	C(5A)-Fe(1A)-C(7A)	70.30(18)
C(6A)-Fe(1A)-C(7A)	40.11(18)	C(4A)-Fe(1A)-C(7A)	78.14(17)
C(3B)-Fe(1B)-C(2B)	92.9(2)	C(3B)-Fe(1B)-C(1B)	98.6(2)
C(2B)-Fe(1B)-C(1B)	96.7(2)	C(3B)-Fe(1B)-C(6B)	95.3(2)
C(2B)-Fe(1B)-C(6B)	122.7(2)	C(1B)-Fe(1B)-C(6B)	137.4(2)
C(3B)-Fe(1B)-C(5B)	127.0(2)	C(2B)-Fe(1B)-C(5B)	93.3(2)
C(1B)-Fe(1B)-C(5B)	132.7(2)	C(6B)-Fe(1B)-C(5B)	40.09(18)
C(3B)-Fe(1B)-C(4B)	165.2(2)	C(2B)-Fe(1B)-C(4B)	93.8(2)
C(1B)-Fe(1B)-C(4B)	93.8(2)	C(6B)-Fe(1B)-C(4B)	70.02(18)
C(5B)-Fe(1B)-C(4B)	39.40(17)	C(3B)-Fe(1B)-C(7B)	91.5(2)
C(2B)-Fe(1B)-C(7B)	162.6(2)	C(1B)-Fe(1B)-C(7B)	99.2(2)
C(6B)-Fe(1B)-C(7B)	40.09(18)	C(5B)-Fe(1B)-C(7B)	70.74(18)
C(4B)-Fe(1B)-C(7B)	78.37(17)	C(2C)-Fe(1C)-C(3C)	92.9(2)
C(2C)-Fe(1C)-C(1C)	97.4(2)	C(3C)-Fe(1C)-C(1C)	99.5(2)
C(2C)-Fe(1C)-C(5C)	92.9(2)	C(3C)-Fe(1C)-C(5C)	126.57(19)
C(1C)-Fe(1C)-C(5C)	132.2(2)	C(2C)-Fe(1C)-C(6C)	122.2(2)
C(3C)-Fe(1C)-C(6C)	94.9(2)	C(1C)-Fe(1C)-C(6C)	137.0(2)
C(5C)-Fe(1C)-C(6C)	40.18(17)	C(2C)-Fe(1C)-C(4C)	93.5(2)
C(3C)-Fe(1C)-C(4C)	165.0(2)	C(1C)-Fe(1C)-C(4C)	93.1(2)
C(5C)-Fe(1C)-C(4C)	39.53(17)	C(6C)-Fe(1C)-C(4C)	70.24(18)
C(2C)-Fe(1C)-C(7C)	162.2(2)	C(3C)-Fe(1C)-C(7C)	91.5(2)
C(1C)-Fe(1C)-C(7C)	99.0(2)	C(5C)-Fe(1C)-C(7C)	70.79(18)
C(6C)-Fe(1C)-C(7C)	40.09(18)	C(4C)-Fe(1C)-C(7C)	78.47(18)
C(2D)-Fe(1D)-C(3D)	93.7(2)	C(2D)-Fe(1D)-C(1D)	97.9(2)
C(3D)-Fe(1D)-C(1D)	98.3(2)	C(2D)-Fe(1D)-C(5D)	92.4(2)
C(3D)-Fe(1D)-C(5D)	127.6(2)	C(1D)-Fe(1D)-C(5D)	132.2(2)
C(2D)-Fe(1D)-C(6D)	120.6(2)	C(3D)-Fe(1D)-C(6D)	95.4(2)
C(1D)-Fe(1D)-C(6D)	138.1(2)	C(5D)-Fe(1D)-C(6D)	39.64(18)
C(2D)-Fe(1D)-C(4D)	94.2(2)	C(3D)-Fe(1D)-C(4D)	165.5(2)
C(1D)-Fe(1D)-C(4D)	92.8(2)	C(5D)-Fe(1D)-C(4D)	39.74(17)
C(6D)-Fe(1D)-C(4D)	70.03(19)	C(2D)-Fe(1D)-C(7D)	160.9(2)
C(3D)-Fe(1D)-C(7D)	90.5(2)	C(1D)-Fe(1D)-C(7D)	100.0(2)
C(5D)-Fe(1D)-C(7D)	70.47(19)	C(6D)-Fe(1D)-C(7D)	40.31(18)
C(4D)-Fe(1D)-C(7D)	78.24(18)	C(2E)-Fe(1E)-C(3E)	93.2(2)
C(2E)-Fe(1E)-C(1E)	98.2(2)	C(3E)-Fe(1E)-C(1E)	98.4(2)
C(2E)-Fe(1E)-C(6E)	120.7(2)	C(3E)-Fe(1E)-C(6E)	95.1(2)
C(1E)-Fe(1E)-C(6E)	137.8(2)	C(2E)-Fe(1E)-C(5E)	92.6(2)
C(3E)-Fe(1E)-C(5E)	127.6(2)	C(1E)-Fe(1E)-C(5E)	132.0(2)
C(6E)-Fe(1E)-C(5E)	39.86(17)	C(2E)-Fe(1E)-C(4E)	94.6(2)
C(3E)-Fe(1E)-C(4E)	165.4(2)	C(1E)-Fe(1E)-C(4E)	92.63(19)
C(6E)-Fe(1E)-C(4E)	70.27(19)	C(5E)-Fe(1E)-C(4E)	39.72(17)
C(2E)-Fe(1E)-C(7E)	160.6(2)	C(3E)-Fe(1E)-C(7E)	90.5(2)
C(1E)-Fe(1E)-C(7E)	100.1(2)	C(6E)-Fe(1E)-C(7E)	39.93(17)
C(5E)-Fe(1E)-C(7E)	70.21(19)	C(4E)-Fe(1E)-C(7E)	78.20(18)
C(9)-O(4)-H(41)	109.5	C(10)-O(6)-C(11)	130.9(6)
C(10)-O(7)-C(12)	135.0(7)	C(9A)-O(4A)-H(42)	109.5
C(10A)-O(6A)-C(11A)	130.5(7)	C(10A)-O(7A)-C(12A)	134.5(6)
C(9B)-O(4B)-H(43)	109.5	C(10B)-O(6B)-C(11B)	130.3(6)
C(10B)-O(7B)-C(12B)	133.0(7)	C(9C)-O(4C)-H(44)	109.5
C(10C)-O(6C)-C(11C)	130.4(7)	C(10C)-O(7C)-C(12C)	133.7(7)
C(9D)-O(4D)-H(45)	109.5	C(10D)-O(6D)-C(11D)	130.5(7)
C(10D)-O(7D)-C(12D)	133.3(6)	C(9E)-O(5E)-H(46)	109.5
C(10E)-O(7E)-C(11E)	130.8(7)	C(10E)-O(8E)-C(12E)	134.0(7)
O(1)-C(1)-Fe(1)	177.9(5)	O(2)-C(2)-Fe(1)	178.1(4)
O(3)-C(3)-Fe(1)	178.4(5)	C(5)-C(4)-C(9)	118.2(4)
C(5)-C(4)-Fe(1)	68.4(3)	C(9)-C(4)-Fe(1)	106.7(3)
C(5)-C(4)-H(4)	124(4)	C(9)-C(4)-H(4)	111(4)
Fe(1)-C(4)-H(4)	123(4)	C(6)-C(5)-C(4)	116.5(4)
C(6)-C(5)-Fe(1)	70.0(3)	C(4)-C(5)-Fe(1)	72.1(3)

C(6)-C(5)-H(5)	120(4)	C(4)-C(5)-H(5)	123(4)
Fe(1)-C(5)-H(5)	120(4)	C(5)-C(6)-C(7)	117.2(4)
C(5)-C(6)-Fe(1)	70.4(2)	C(7)-C(6)-Fe(1)	72.9(3)
C(5)-C(6)-H(6)	126(4)	C(7)-C(6)-H(6)	116(4)
Fe(1)-C(6)-H(6)	123(4)	C(6)-C(7)-C(8)	121.9(4)
C(6)-C(7)-Fe(1)	67.3(2)	C(8)-C(7)-Fe(1)	98.6(3)
C(6)-C(7)-H(7)	118(4)	C(8)-C(7)-H(7)	118(4)
Fe(1)-C(7)-H(7)	120(4)	O(5)-C(8)-C(7)	125.2(4)
O(5)-C(8)-C(9)	119.0(4)	C(7)-C(8)-C(9)	115.5(4)
O(4)-C(9)-C(10)	110.4(3)	O(4)-C(9)-C(4)	108.0(3)
C(10)-C(9)-C(4)	111.4(3)	O(4)-C(9)-C(8)	108.8(3)
C(10)-C(9)-C(8)	109.9(3)	C(4)-C(9)-C(8)	108.2(3)
O(7)-C(10)-O(6)	125.8(5)	O(7)-C(10)-C(9)	116.1(4)
O(6)-C(10)-C(9)	118.1(4)	O(6)-C(11)-H(11A)	109.5
O(6)-C(11)-H(11B)	109.5	O(6)-C(11)-H(11C)	109.5
O(7)-C(12)-H(12A)	109.5	O(7)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	O(7)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
O(1A)-C(1A)-Fe(1A)	177.9(5)	O(2A)-C(2A)-Fe(1A)	179.7(5)
O(3A)-C(3A)-Fe(1A)	177.9(5)	C(5A)-C(4A)-C(9A)	118.8(4)
C(5A)-C(4A)-Fe(1A)	67.9(3)	C(9A)-C(4A)-Fe(1A)	106.4(3)
C(5A)-C(4A)-H(4A)	121(4)	C(9A)-C(4A)-H(4A)	113(4)
Fe(1A)-C(4A)-H(4A)	122(4)	C(6A)-C(5A)-C(4A)	116.8(4)
C(6A)-C(5A)-Fe(1A)	70.1(3)	C(4A)-C(5A)-Fe(1A)	72.4(3)
C(6A)-C(5A)-H(5A)	116(4)	C(4A)-C(5A)-H(5A)	127(4)
Fe(1A)-C(5A)-H(5A)	120(4)	C(5A)-C(6A)-C(7A)	116.2(4)
C(5A)-C(6A)-Fe(1A)	70.0(3)	C(7A)-C(6A)-Fe(1A)	72.6(3)
C(5A)-C(6A)-H(6A)	123(4)	C(7A)-C(6A)-H(6A)	121(4)
Fe(1A)-C(6A)-H(6A)	124(4)	C(6A)-C(7A)-C(8A)	123.0(4)
C(6A)-C(7A)-Fe(1A)	67.3(3)	C(8A)-C(7A)-Fe(1A)	98.5(3)
C(6A)-C(7A)-H(7A)	122(4)	C(8A)-C(7A)-H(7A)	113(4)
Fe(1A)-C(7A)-H(7A)	121(4)	O(5A)-C(8A)-C(7A)	126.1(4)
O(5A)-C(8A)-C(9A)	117.9(4)	C(7A)-C(8A)-C(9A)	115.7(4)
O(4A)-C(9A)-C(4A)	108.4(4)	O(4A)-C(9A)-C(8A)	109.5(3)
C(4A)-C(9A)-C(8A)	108.2(3)	O(4A)-C(9A)-C(10A)	110.6(3)
C(4A)-C(9A)-C(10A)	110.7(4)	C(8A)-C(9A)-C(10A)	109.4(3)
O(7A)-C(10A)-O(6A)	126.2(5)	O(7A)-C(10A)-C(9A)	116.5(4)
O(6A)-C(10A)-C(9A)	117.3(4)	O(6A)-C(11A)-H(11D)	109.5
O(6A)-C(11A)-H(11E)	109.5	H(11D)-C(11A)-H(11E)	109.5
O(6A)-C(11A)-H(11F)	109.5	H(11D)-C(11A)-H(11F)	109.5
H(11E)-C(11A)-H(11F)	109.5	O(7A)-C(12A)-H(12D)	109.5
O(7A)-C(12A)-H(12E)	109.5	O(7A)-C(12A)-H(12F)	109.5
O(1B)-C(1B)-Fe(1B)	177.8(5)	O(2B)-C(2B)-Fe(1B)	178.7(5)
O(3B)-C(3B)-Fe(1B)	178.8(5)	C(5B)-C(4B)-C(9B)	119.4(4)
C(5B)-C(4B)-Fe(1B)	68.5(3)	C(9B)-C(4B)-Fe(1B)	106.8(3)
C(5B)-C(4B)-H(4B)	121(4)	C(9B)-C(4B)-H(4B)	113(4)
Fe(1B)-C(4B)-H(4B)	121(4)	C(4B)-C(5B)-C(6B)	116.1(4)
C(4B)-C(5B)-Fe(1B)	72.1(3)	C(6B)-C(5B)-Fe(1B)	69.9(3)
C(4B)-C(5B)-H(5B)	119(4)	C(6B)-C(5B)-H(5B)	125(4)
Fe(1B)-C(5B)-H(5B)	127(4)	C(5B)-C(6B)-C(7B)	116.7(4)
C(5B)-C(6B)-Fe(1B)	70.0(3)	C(7B)-C(6B)-Fe(1B)	72.6(3)
C(5B)-C(6B)-H(6B)	127(4)	C(7B)-C(6B)-H(6B)	115(4)
Fe(1B)-C(6B)-H(6B)	117(4)	C(6B)-C(7B)-C(8B)	121.6(4)
C(6B)-C(7B)-Fe(1B)	67.3(2)	C(8B)-C(7B)-Fe(1B)	98.2(3)
C(6B)-C(7B)-H(7B)	118(4)	C(8B)-C(7B)-H(7B)	117(4)
Fe(1B)-C(7B)-H(7B)	124(4)	O(5B)-C(8B)-C(7B)	124.6(4)
O(5B)-C(8B)-C(9B)	118.6(4)	C(7B)-C(8B)-C(9B)	116.5(4)
O(4B)-C(9B)-C(4B)	108.6(3)	O(4B)-C(9B)-C(10B)	110.2(3)
C(4B)-C(9B)-C(10B)	110.9(3)	O(4B)-C(9B)-C(8B)	109.5(3)
C(4B)-C(9B)-C(8B)	107.8(3)	C(10B)-C(9B)-C(8B)	109.8(4)
O(6B)-C(10B)-O(7B)	126.4(5)	O(6B)-C(10B)-C(9B)	118.1(4)
O(7B)-C(10B)-C(9B)	115.5(4)	O(6B)-C(11B)-H(11G)	109.5
O(6B)-C(11B)-H(11H)	109.5	H(11G)-C(11B)-H(11H)	109.5
O(6B)-C(11B)-H(11I)	109.5	H(11G)-C(11B)-H(11I)	109.5
H(11H)-C(11B)-H(11I)	109.5	O(7B)-C(12B)-H(12G)	109.5
O(7B)-C(12B)-H(12H)	109.5	O(7B)-C(12B)-H(12I)	109.5
O(1C)-C(1C)-Fe(1C)	178.9(5)	O(2C)-C(2C)-Fe(1C)	178.7(5)
O(3C)-C(3C)-Fe(1C)	178.8(5)	C(5C)-C(4C)-C(9C)	119.2(4)
C(5C)-C(4C)-Fe(1C)	68.4(3)	C(9C)-C(4C)-Fe(1C)	107.1(3)
C(5C)-C(4C)-H(4C)	120(4)	C(9C)-C(4C)-H(4C)	113(4)

Fe(1C)-C(4C)-H(4C)	122(4)	C(4C)-C(5C)-C(6C)	116.2(4)
C(4C)-C(5C)-Fe(1C)	72.0(3)	C(6C)-C(5C)-Fe(1C)	70.1(2)
C(4C)-C(5C)-H(5C)	122(4)	C(6C)-C(5C)-H(5C)	121(4)
Fe(1C)-C(5C)-H(5C)	120(4)	C(5C)-C(6C)-C(7C)	116.5(4)
C(5C)-C(6C)-Fe(1C)	69.7(2)	C(7C)-C(6C)-Fe(1C)	72.6(3)
C(5C)-C(6C)-H(6C)	123(3)	C(7C)-C(6C)-H(6C)	119(4)
Fe(1C)-C(6C)-H(6C)	115(4)	C(8C)-C(7C)-C(6C)	121.6(4)
C(8C)-C(7C)-Fe(1C)	97.8(3)	C(6C)-C(7C)-Fe(1C)	67.3(2)
C(8C)-C(7C)-H(7C)	121(4)	C(6C)-C(7C)-H(7C)	115(4)
Fe(1C)-C(7C)-H(7C)	116(4)	O(5C)-C(8C)-C(7C)	124.9(4)
O(5C)-C(8C)-C(9C)	117.7(4)	C(7C)-C(8C)-C(9C)	117.2(4)
O(4C)-C(9C)-C(4C)	108.4(3)	O(4C)-C(9C)-C(10C)	111.1(3)
C(4C)-C(9C)-C(10C)	111.2(3)	O(4C)-C(9C)-C(8C)	109.3(3)
C(4C)-C(9C)-C(8C)	107.0(3)	C(10C)-C(9C)-C(8C)	109.7(3)
O(7C)-C(10C)-O(6C)	125.8(5)	O(7C)-C(10C)-C(9C)	116.6(4)
O(6C)-C(10C)-C(9C)	117.6(4)	O(6C)-C(11C)-H(11J)	109.5
O(6C)-C(11C)-H(11K)	109.5	O(6C)-C(11C)-H(11L)	109.5
O(7C)-C(12C)-H(12J)	109.5	O(7C)-C(12C)-H(12K)	109.5
H(12J)-C(12C)-H(12K)	109.5	O(7C)-C(12C)-H(12L)	109.5
H(12J)-C(12C)-H(12L)	109.5	H(12K)-C(12C)-H(12L)	109.5
O(1D)-C(1D)-Fe(1D)	178.3(5)	O(2D)-C(2D)-Fe(1D)	179.4(5)
O(3D)-C(3D)-Fe(1D)	178.7(5)	C(5D)-C(4D)-C(9D)	118.9(4)
C(5D)-C(4D)-Fe(1D)	67.9(3)	C(9D)-C(4D)-Fe(1D)	107.0(3)
C(5D)-C(4D)-H(4D)	127(4)	C(9D)-C(4D)-H(4D)	108(4)
Fe(1D)-C(4D)-H(4D)	122(4)	C(6D)-C(5D)-C(4D)	116.7(4)
C(6D)-C(5D)-Fe(1D)	70.4(3)	C(4D)-C(5D)-Fe(1D)	72.4(3)
C(6D)-C(5D)-H(5D)	121(4)	C(4D)-C(5D)-H(5D)	123(4)
Fe(1D)-C(5D)-H(5D)	127(4)	C(5D)-C(6D)-C(7D)	116.2(4)
C(5D)-C(6D)-Fe(1D)	70.0(3)	C(7D)-C(6D)-Fe(1D)	72.1(3)
C(5D)-C(6D)-H(6D)	126(4)	C(7D)-C(6D)-H(6D)	118(4)
Fe(1D)-C(6D)-H(6D)	122(4)	C(8D)-C(7D)-C(6D)	122.6(4)
C(8D)-C(7D)-Fe(1D)	99.0(3)	C(6D)-C(7D)-Fe(1D)	67.6(3)
C(8D)-C(7D)-H(7D)	113(4)	C(6D)-C(7D)-H(7D)	122(4)
Fe(1D)-C(7D)-H(7D)	119(4)	O(5D)-C(8D)-C(7D)	125.8(4)
O(5D)-C(8D)-C(9D)	118.0(4)	C(7D)-C(8D)-C(9D)	115.8(4)
O(4D)-C(9D)-C(4D)	108.4(3)	O(4D)-C(9D)-C(10D)	110.9(3)
C(4D)-C(9D)-C(10D)	111.2(3)	O(4D)-C(9D)-C(8D)	109.0(3)
C(4D)-C(9D)-C(8D)	107.3(3)	C(10D)-C(9D)-C(8D)	109.9(3)
O(6D)-C(10D)-O(7D)	126.9(5)	O(6D)-C(10D)-C(9D)	117.6(4)
O(7D)-C(10D)-C(9D)	115.4(4)	O(6D)-C(11D)-H(11M)	109.5
O(6D)-C(11D)-H(11N)	109.5	O(6D)-C(11D)-H(11O)	109.5
O(7D)-C(12D)-H(12M)	109.5	O(7D)-C(12D)-H(12N)	109.5
H(12M)-C(12D)-H(12N)	109.5	O(7D)-C(12D)-H(12O)	109.5
H(12M)-C(12D)-H(12O)	109.5	H(12N)-C(12D)-H(12O)	109.5
O(2E)-C(1E)-Fe(1E)	178.4(5)	O(3E)-C(2E)-Fe(1E)	179.5(5)
O(4E)-C(3E)-Fe(1E)	178.5(5)	C(5E)-C(4E)-C(9E)	118.7(4)
C(5E)-C(4E)-Fe(1E)	68.7(3)	C(9E)-C(4E)-Fe(1E)	106.8(3)
C(5E)-C(4E)-H(4E)	117(4)	C(9E)-C(4E)-H(4E)	114(4)
Fe(1E)-C(4E)-H(4E)	124(4)	C(6E)-C(5E)-C(4E)	116.2(4)
C(6E)-C(5E)-Fe(1E)	69.8(3)	C(4E)-C(5E)-Fe(1E)	71.6(3)
C(6E)-C(5E)-H(5E)	122(4)	C(4E)-C(5E)-H(5E)	122(4)
Fe(1E)-C(5E)-H(5E)	122(4)	C(5E)-C(6E)-C(7E)	116.4(4)
C(5E)-C(6E)-Fe(1E)	70.3(3)	C(7E)-C(6E)-Fe(1E)	72.4(3)
C(5E)-C(6E)-H(6E)	127(4)	C(7E)-C(6E)-H(6E)	117(4)
Fe(1E)-C(6E)-H(6E)	124(4)	C(6E)-C(7E)-C(8E)	122.3(4)
C(6E)-C(7E)-Fe(1E)	67.6(3)	C(8E)-C(7E)-Fe(1E)	98.1(3)
C(6E)-C(7E)-H(7E)	120(4)	C(8E)-C(7E)-H(7E)	116(4)
Fe(1E)-C(7E)-H(7E)	117(5)	O(6E)-C(8E)-C(7E)	124.6(4)
O(6E)-C(8E)-C(9E)	118.6(4)	C(7E)-C(8E)-C(9E)	116.5(4)
O(5E)-C(9E)-C(4E)	108.6(3)	O(5E)-C(9E)-C(8E)	109.6(3)
C(4E)-C(9E)-C(8E)	107.6(3)	O(5E)-C(9E)-C(10E)	110.4(4)
C(4E)-C(9E)-C(10E)	110.7(3)	C(8E)-C(9E)-C(10E)	110.0(4)
O(8E)-C(10E)-O(7E)	127.0(5)	O(8E)-C(10E)-C(9E)	116.0(4)
O(7E)-C(10E)-C(9E)	117.1(4)	O(7E)-C(11E)-H(11P)	109.5
O(7E)-C(11E)-H(11Q)	109.5	O(7E)-C(11E)-H(11R)	109.5
O(8E)-C(12E)-H(12P)	109.5	O(8E)-C(12E)-H(12Q)	109.5
H(12P)-C(12E)-H(12Q)	109.5	O(8E)-C(12E)-H(12R)	109.5
H(12P)-C(12E)-H(12R)	109.5	H(12Q)-C(12E)-H(12R)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 21 Anisotropic displacement parameters ($Å^2$ x 10^3) for 396. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	19(1)	16(1)	19(1)	-1(1)	0(1)	-6(1)
Fe(1A)	18(1)	22(1)	19(1)	-1(1)	-2(1)	-11(1)
Fe(1B)	19(1)	22(1)	19(1)	-1(1)	-2(1)	-10(1)
Fe(1C)	21(1)	18(1)	18(1)	0(1)	-1(1)	-10(1)
Fe(1D)	22(1)	19(1)	19(1)	0(1)	-1(1)	-11(1)
Fe(1E)	18(1)	20(1)	19(1)	-2(1)	0(1)	-7(1)
O(1)	36(2)	37(2)	25(2)	6(2)	-8(2)	-9(2)
O(2)	56(3)	33(2)	37(3)	-16(2)	0(2)	-23(2)
O(3)	29(2)	46(3)	39(3)	4(2)	8(2)	-14(2)
O(4)	18(2)	20(2)	34(2)	7(2)	-9(1)	-7(1)
O(5)	27(2)	13(2)	40(2)	-3(2)	2(2)	-8(2)
O(6)	54(3)	58(3)	73(3)	-15(2)	43(2)	-27(2)
O(7)	84(3)	45(3)	25(2)	-1(2)	-11(2)	-29(2)
O(1A)	38(2)	61(3)	26(2)	-1(2)	6(2)	-34(2)
O(2A)	47(3)	44(2)	33(2)	-15(2)	6(2)	-33(2)
O(3A)	39(2)	46(3)	50(3)	10(2)	-23(2)	-12(2)
O(4A)	15(2)	22(2)	39(2)	-2(2)	4(1)	-10(2)
O(5A)	28(2)	21(2)	39(2)	0(2)	-7(2)	-17(2)
O(6A)	60(3)	63(3)	75(3)	31(2)	-50(2)	-28(2)
O(7A)	81(3)	63(3)	28(2)	-10(2)	14(2)	-49(3)
O(1B)	34(2)	60(3)	21(2)	-7(2)	11(2)	-28(2)
O(2B)	30(2)	36(2)	38(3)	12(2)	-18(2)	-4(2)
O(3B)	54(3)	42(2)	40(3)	-14(2)	3(2)	-36(2)
O(4B)	18(2)	23(2)	36(2)	-3(2)	4(2)	-12(2)
O(5B)	15(2)	22(2)	35(2)	-3(2)	-4(2)	-5(2)
O(6B)	60(3)	73(3)	68(3)	-33(2)	-13(2)	-37(2)
O(7B)	45(2)	64(3)	22(2)	6(2)	1(2)	-12(2)
O(1C)	59(3)	38(2)	25(2)	-13(2)	6(2)	-30(2)
O(2C)	41(2)	29(2)	40(3)	13(2)	-14(2)	-8(2)
O(3C)	44(2)	55(3)	41(3)	-6(2)	13(2)	-39(2)
O(4C)	24(2)	16(2)	33(2)	-6(2)	1(2)	-12(2)
O(5C)	21(2)	15(2)	33(2)	-3(2)	5(1)	-5(2)
O(6C)	62(3)	54(3)	64(3)	8(2)	31(2)	-33(2)
O(7C)	70(3)	47(3)	24(2)	-8(2)	-10(2)	-17(2)
O(1D)	65(3)	41(2)	27(2)	-10(2)	-2(2)	-35(2)
O(2D)	46(3)	52(3)	33(2)	-6(2)	10(2)	-35(2)
O(3D)	47(3)	38(2)	45(3)	21(2)	-18(2)	-13(2)
O(4D)	21(2)	16(2)	37(2)	-7(1)	-3(2)	-8(1)
O(5D)	23(2)	27(2)	38(2)	4(2)	-7(2)	-18(2)
O(6D)	69(3)	50(3)	78(3)	49(2)	-39(2)	-29(2)
O(7D)	68(3)	88(3)	23(2)	-7(2)	6(2)	-57(3)
O(2E)	31(2)	38(2)	27(2)	9(2)	-13(2)	-6(2)
O(3E)	25(2)	51(3)	33(2)	8(2)	4(2)	-16(2)
O(4E)	63(3)	38(3)	48(3)	-25(2)	7(2)	-24(2)
O(5E)	18(2)	16(2)	38(2)	3(1)	-8(2)	-5(1)
O(6E)	13(2)	25(2)	39(2)	-6(2)	-2(1)	-6(2)
O(7E)	60(3)	63(3)	83(3)	-59(3)	15(2)	-26(2)
O(8E)	48(2)	88(3)	23(2)	11(2)	-6(2)	-32(2)
C(1)	35(3)	23(3)	21(3)	-6(2)	0(2)	-15(3)
C(2)	19(3)	30(3)	29(3)	3(3)	0(2)	-8(2)
C(3)	23(3)	25(3)	25(3)	1(2)	-3(2)	-9(2)
C(4)	20(3)	16(3)	16(2)	0(2)	1(2)	-8(2)
C(5)	20(2)	11(2)	20(2)	2(2)	0(2)	-3(2)
C(6)	19(3)	18(3)	24(3)	-4(2)	-2(2)	-5(2)
C(7)	15(2)	18(3)	23(3)	-8(2)	5(2)	-8(2)
C(8)	23(2)	17(3)	14(2)	-6(2)	2(2)	-8(2)
C(9)	13(2)	13(2)	23(2)	1(2)	-2(2)	-4(2)
C(10)	24(3)	12(2)	26(3)	-2(2)	5(2)	-7(2)
C(11)	40(6)	55(8)	23(6)	-4(5)	13(5)	-19(6)
C(12)	79(9)	45(7)	23(6)	8(5)	2(6)	-40(7)
C(1A)	30(3)	25(3)	20(3)	1(2)	-5(2)	-13(2)
C(2A)	19(3)	36(3)	19(3)	-1(2)	4(2)	-15(2)
C(3A)	31(3)	38(3)	28(3)	3(2)	-8(2)	-20(3)

C(4A)	17(2)	15(2)	18(2)	-1(2)	1(2)	-9(2)
C(5A)	19(3)	30(3)	17(2)	-1(2)	-1(2)	-16(2)
C(6A)	15(2)	32(3)	18(2)	-4(2)	3(2)	-12(2)
C(7A)	16(3)	20(3)	23(3)	-3(2)	-2(2)	-7(2)
C(8A)	21(3)	15(2)	16(2)	-4(2)	-1(2)	-8(2)
C(9A)	14(2)	21(3)	20(2)	1(2)	2(2)	-9(2)
C(10A)	28(3)	22(3)	29(3)	3(2)	-10(2)	-18(2)
C(11A)	44(7)	67(8)	39(7)	28(6)	-28(6)	-35(6)
C(12A)	76(8)	51(7)	3(5)	2(5)	1(5)	-40(7)
C(1B)	28(3)	22(3)	21(3)	1(2)	-9(2)	-10(2)
C(2B)	29(3)	38(3)	21(3)	-4(2)	1(2)	-21(3)
C(3B)	21(3)	37(3)	28(3)	-2(2)	4(2)	-14(2)
C(4B)	17(2)	16(3)	21(3)	-1(2)	3(2)	-7(2)
C(5B)	16(2)	21(3)	17(2)	-2(2)	-2(2)	-7(2)
C(6B)	25(3)	33(3)	15(2)	5(2)	-6(2)	-20(2)
C(7B)	15(2)	18(3)	26(3)	-2(2)	-3(2)	-7(2)
C(8B)	24(3)	25(3)	14(2)	4(2)	-6(2)	-11(2)
C(9B)	18(2)	17(2)	22(2)	-4(2)	1(2)	-12(2)
C(10B)	15(2)	22(3)	25(3)	-2(2)	-4(2)	-2(2)
C(11B)	48(7)	71(8)	24(6)	-24(6)	-1(5)	-41(6)
C(12B)	56(8)	51(8)	22(6)	-14(5)	5(5)	-16(6)
C(1C)	27(3)	32(3)	14(3)	2(2)	-2(2)	-16(3)
C(2C)	37(3)	29(3)	29(3)	2(2)	-2(2)	-22(3)
C(3C)	30(3)	24(3)	31(3)	-8(2)	-3(2)	-10(2)
C(4C)	14(2)	20(3)	19(3)	-2(2)	3(2)	-8(2)
C(5C)	22(3)	16(3)	22(3)	-2(2)	2(2)	-7(2)
C(6C)	32(3)	26(3)	13(2)	6(2)	-7(2)	-18(2)
C(7C)	23(3)	17(3)	24(3)	4(2)	-6(2)	-11(2)
C(8C)	23(2)	20(3)	11(2)	2(2)	-3(2)	-8(2)
C(9C)	15(2)	12(2)	23(2)	-4(2)	1(2)	-5(2)
C(10C)	21(2)	10(2)	27(3)	2(2)	5(2)	-1(2)
C(11C)	79(8)	48(7)	25(6)	7(5)	20(6)	-47(7)
C(12C)	58(8)	52(8)	16(6)	-1(5)	2(5)	-14(6)
C(1D)	27(3)	29(3)	21(3)	11(2)	-2(2)	-16(3)
C(2D)	36(3)	24(3)	20(3)	-3(2)	-2(2)	-18(3)
C(3D)	31(3)	33(3)	29(3)	-1(2)	1(2)	-18(3)
C(4D)	17(2)	22(3)	18(2)	-1(2)	-3(2)	-11(2)
C(5D)	28(3)	21(3)	18(2)	-2(2)	-2(2)	-18(2)
C(6D)	27(3)	19(3)	19(3)	-4(2)	2(2)	-10(2)
C(7D)	16(3)	17(3)	21(3)	-2(2)	5(2)	-7(2)
C(8D)	17(2)	27(3)	10(2)	1(2)	3(2)	-13(2)
C(9D)	17(2)	12(2)	22(2)	-1(2)	-1(2)	-8(2)
C(10D)	21(2)	26(3)	26(3)	4(2)	-4(2)	-16(2)
C(11D)	75(9)	36(7)	26(6)	20(5)	-19(6)	-22(6)
C(12D)	41(6)	66(8)	18(6)	2(5)	-9(5)	-32(6)
C(1E)	17(3)	30(3)	19(3)	-11(2)	5(2)	-8(2)
C(2E)	25(3)	27(3)	27(3)	4(2)	-6(2)	-11(2)
C(3E)	26(3)	35(3)	31(3)	-2(3)	3(2)	-15(3)
C(4E)	17(2)	16(3)	22(2)	1(2)	-2(2)	-8(2)
C(5E)	16(2)	24(3)	15(2)	-2(2)	2(2)	-6(2)
C(6E)	21(3)	16(3)	20(2)	-2(2)	3(2)	-5(2)
C(7E)	27(3)	16(3)	23(3)	-1(2)	2(2)	-10(2)
C(8E)	15(2)	25(3)	16(2)	-1(2)	-1(2)	-10(2)
C(9E)	15(2)	13(2)	23(2)	-2(2)	-3(2)	-3(2)
C(10E)	14(2)	29(3)	32(3)	-6(2)	-1(2)	-11(2)
C(11E)	64(8)	45(7)	24(6)	-13(5)	-3(6)	-21(6)
C(12E)	52(7)	71(8)	17(6)	-3(5)	6(5)	-36(7)

Table 22 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 396

Atom	x	y	z	U(eq)
H(41)	5052	8556	196	34(16)
H(42)	4326	-199	1976	22(14)
H(43)	9405	2651	3553	47(18)
H(44)	591	10238	5317	48(18)

H(45)	6681	4231	6870	22(14)
H(46)	14335	3649	8658	16(13)
H(11A)	4038	5951	1175	64
H(11B)	1651	7387	1016	64
H(11C)	2938	8671	1119	64
H(12A)	6784	6203	1284	69
H(12B)	9540	4839	1257	69
H(12C)	8141	3483	1245	69
H(11D)	3630	3675	1058	70
H(11E)	1484	3404	1183	70
H(11F)	3668	1283	1037	70
H(12D)	7206	-527	915	60
H(12E)	9800	-1088	949	60
H(12F)	7742	1520	948	60
H(11G)	6624	5529	4494	63
H(11H)	8530	6097	4347	63
H(11I)	9263	3545	4470	63
H(12G)	7232	1757	4615	70
H(12H)	5354	964	4591	70
H(12I)	4571	3643	4585	70
H(11J)	4639	8047	4401	68
H(11K)	4050	10493	4511	68
H(11L)	2130	10227	4359	68
H(12J)	648	8688	4247	73
H(12K)	-470	7050	4271	73
H(12L)	2263	5958	4282	73
H(11M)	9511	3235	7828	73
H(11N)	10304	866	7678	73
H(11O)	7696	2373	7796	73
H(12M)	6197	6027	7946	59
H(12N)	4894	8778	7920	59
H(12O)	7651	7343	7905	59
H(11P)	12178	2762	7728	69
H(11Q)	14506	708	7856	69
H(11R)	14482	2942	7705	69
H(12P)	12699	6108	7575	66
H(12Q)	11411	8842	7599	66
H(12R)	9946	7539	7607	66
H(4)	7470(80)	2950(100)	266(14)	80
H(5)	11380(100)	350(20)	447(14)	80
H(6)	13840(30)	2120(90)	465(13)	80
H(7)	12390(80)	5890(100)	291(14)	80
H(4A)	6970(80)	2900(30)	1928(14)	80
H(5A)	11060(90)	1430(90)	1745(14)	80
H(6A)	13430(30)	-2610(90)	1726(13)	80
H(7A)	11700(90)	-4964(19)	1907(14)	80
H(4B)	3700(100)	5700(30)	3598(14)	80
H(5B)	1190(40)	4350(80)	3798(13)	80
H(6B)	2860(90)	-30(90)	3778(14)	80
H(7B)	6710(90)	-2200(20)	3640(14)	80
H(4C)	3730(30)	4570(100)	5259(14)	80
H(5C)	2390(80)	2140(30)	5081(14)	80
H(6C)	-1820(90)	3770(80)	5085(14)	80
H(7C)	-4140(30)	7500(100)	5245(14)	80
H(4D)	9640(110)	6730(110)	6929(15)	80
H(5D)	8270(110)	10530(100)	7130(14)	80
H(6D)	4090(100)	13060(110)	7126(14)	80
H(7D)	1980(110)	11410(110)	6948(15)	80
H(4E)	8630(100)	6240(110)	8579(14)	80
H(5E)	6370(110)	10100(100)	8410(14)	80
H(6E)	8100(100)	12650(110)	8395(14)	80
H(7E)	11750(110)	10870(110)	8582(15)	80

Table 23 Dihedral angles [^{o}] for 396

Atom1 - Atom2 - Atom3 - Atom4	Dihedral

C(2) - Fe(1) - C(1) - O(1)	173(100)
C(3) - Fe(1) - C(1) - O(1)	-93(15)
C(6) - Fe(1) - C(1) - O(1)	15(15)
C(5) - Fe(1) - C(1) - O(1)	72(15)
C(4) - Fe(1) - C(1) - O(1)	79(15)
C(7) - Fe(1) - C(1) - O(1)	0(15)
C(3) - Fe(1) - C(2) - O(2)	-148(14)
C(1) - Fe(1) - C(2) - O(2)	-48(14)
C(6) - Fe(1) - C(2) - O(2)	115(14)
C(5) - Fe(1) - C(2) - O(2)	86(14)
C(4) - Fe(1) - C(2) - O(2)	46(14)
C(7) - Fe(1) - C(2) - O(2)	109(14)
C(2) - Fe(1) - C(3) - O(3)	157(100)
C(1) - Fe(1) - C(3) - O(3)	59(16)
C(6) - Fe(1) - C(3) - O(3)	-80(16)
C(5) - Fe(1) - C(3) - O(3)	-107(16)
C(4) - Fe(1) - C(3) - O(3)	-89(16)
C(7) - Fe(1) - C(3) - O(3)	-40(16)
C(2) - Fe(1) - C(4) - C(5)	91.0(3)
C(3) - Fe(1) - C(4) - C(5)	-23.2(9)
C(1) - Fe(1) - C(4) - C(5)	-171.7(3)
C(6) - Fe(1) - C(4) - C(5)	-32.4(3)
C(7) - Fe(1) - C(4) - C(5)	-72.9(3)
C(2) - Fe(1) - C(4) - C(9)	-154.8(3)
C(3) - Fe(1) - C(4) - C(9)	91.0(8)
C(1) - Fe(1) - C(4) - C(9)	-57.4(3)
C(6) - Fe(1) - C(4) - C(9)	81.9(3)
C(5) - Fe(1) - C(4) - C(9)	114.3(4)
C(7) - Fe(1) - C(4) - C(9)	41.3(3)
C(9) - C(4) - C(5) - C(6)	-42.2(6)
Fe(1) - C(4) - C(5) - C(6)	55.8(4)
C(9) - C(4) - C(5) - Fe(1)	-98.0(4)
C(2) - Fe(1) - C(5) - C(6)	140.4(3)
C(3) - Fe(1) - C(5) - C(6)	44.7(3)
C(1) - Fe(1) - C(5) - C(6)	-116.8(3)
C(4) - Fe(1) - C(5) - C(6)	-128.0(4)
C(7) - Fe(1) - C(5) - C(6)	-32.3(3)
C(2) - Fe(1) - C(5) - C(4)	-91.5(3)
C(3) - Fe(1) - C(5) - C(4)	172.7(3)
C(1) - Fe(1) - C(5) - C(4)	11.2(4)
C(6) - Fe(1) - C(5) - C(4)	128.0(4)
C(7) - Fe(1) - C(5) - C(4)	95.7(3)
C(4) - C(5) - C(6) - C(7)	0.7(6)
Fe(1) - C(5) - C(6) - C(7)	57.6(4)
C(4) - C(5) - C(6) - Fe(1)	-56.9(4)
C(2) - Fe(1) - C(6) - C(5)	-48.9(3)
C(3) - Fe(1) - C(6) - C(5)	-145.4(3)
C(1) - Fe(1) - C(6) - C(5)	104.8(4)
C(4) - Fe(1) - C(6) - C(5)	32.2(3)
C(7) - Fe(1) - C(6) - C(5)	128.2(4)
C(2) - Fe(1) - C(6) - C(7)	-177.1(3)
C(3) - Fe(1) - C(6) - C(7)	86.4(3)
C(1) - Fe(1) - C(6) - C(7)	-23.4(4)
C(5) - Fe(1) - C(6) - C(7)	-128.2(4)
C(4) - Fe(1) - C(6) - C(7)	-96.0(3)
C(5) - C(6) - C(7) - C(8)	29.7(6)
Fe(1) - C(6) - C(7) - C(8)	86.0(4)
C(5) - C(6) - C(7) - Fe(1)	-56.4(4)
C(2) - Fe(1) - C(7) - C(6)	7.9(7)
C(3) - Fe(1) - C(7) - C(6)	-96.2(3)
C(1) - Fe(1) - C(7) - C(6)	164.1(3)
C(5) - Fe(1) - C(7) - C(6)	32.2(3)
C(4) - Fe(1) - C(7) - C(6)	72.5(3)
C(2) - Fe(1) - C(7) - C(8)	-113.2(6)
C(3) - Fe(1) - C(7) - C(8)	142.7(3)
C(1) - Fe(1) - C(7) - C(8)	42.9(3)
C(6) - Fe(1) - C(7) - C(8)	-121.1(4)
C(5) - Fe(1) - C(7) - C(8)	-88.9(3)
C(4) - Fe(1) - C(7) - C(8)	-48.7(3)

C(6) - C(7) - C(8) - O(5)	168.6(4)
Fe(1) - C(7) - C(8) - O(5)	-122.8(4)
C(6) - C(7) - C(8) - C(9)	-17.7(6)
Fe(1) - C(7) - C(8) - C(9)	50.9(4)
C(5) - C(4) - C(9) - O(4)	168.2(4)
Fe(1) - C(4) - C(9) - O(4)	94.2(3)
C(5) - C(4) - C(9) - C(10)	-70.5(5)
Fe(1) - C(4) - C(9) - C(10)	-144.4(3)
C(5) - C(4) - C(9) - C(8)	50.5(5)
Fe(1) - C(4) - C(9) - C(8)	-23.5(4)
O(5) - C(8) - C(9) - O(4)	37.3(5)
C(7) - C(8) - C(9) - O(4)	-136.8(4)
O(5) - C(8) - C(9) - C(10)	-83.7(5)
C(7) - C(8) - C(9) - C(10)	102.2(4)
O(5) - C(8) - C(9) - C(4)	154.4(4)
C(7) - C(8) - C(9) - C(4)	-19.7(5)
C(12) - O(7) - C(10) - O(6)	5.2(10)
C(12) - O(7) - C(10) - C(9)	-174.4(7)
C(11) - O(6) - C(10) - O(7)	1.6(10)
C(11) - O(6) - C(10) - C(9)	-178.8(8)
O(4) - C(9) - C(10) - O(7)	-170.2(4)
C(4) - C(9) - C(10) - O(7)	69.8(5)
C(8) - C(9) - C(10) - O(7)	-50.2(5)
O(4) - C(9) - C(10) - O(6)	10.2(5)
C(4) - C(9) - C(10) - O(6)	-109.8(4)
C(8) - C(9) - C(10) - O(6)	130.2(4)
C(2A) - Fe(1A) - C(1A) - O(1A)	-178(100)
C(3A) - Fe(1A) - C(1A) - O(1A)	-83(14)
C(5A) - Fe(1A) - C(1A) - O(1A)	82(14)
C(6A) - Fe(1A) - C(1A) - O(1A)	25(15)
C(4A) - Fe(1A) - C(1A) - O(1A)	88(14)
C(7A) - Fe(1A) - C(1A) - O(1A)	9(14)
C(3A) - Fe(1A) - C(2A) - O(2A)	109(100)
C(1A) - Fe(1A) - C(2A) - O(2A)	-152(100)
C(5A) - Fe(1A) - C(2A) - O(2A)	-19(100)
C(6A) - Fe(1A) - C(2A) - O(2A)	11(100)
C(4A) - Fe(1A) - C(2A) - O(2A)	-59(100)
C(7A) - Fe(1A) - C(2A) - O(2A)	8(100)
C(2A) - Fe(1A) - C(3A) - O(3A)	132(14)
C(1A) - Fe(1A) - C(3A) - O(3A)	33(14)
C(5A) - Fe(1A) - C(3A) - O(3A)	-132(14)
C(6A) - Fe(1A) - C(3A) - O(3A)	-107(14)
C(4A) - Fe(1A) - C(3A) - O(3A)	-107(14)
C(7A) - Fe(1A) - C(3A) - O(3A)	-67(14)
C(2A) - Fe(1A) - C(4A) - C(5A)	88.6(3)
C(3A) - Fe(1A) - C(4A) - C(5A)	-32.7(9)
C(1A) - Fe(1A) - C(4A) - C(5A)	-173.2(3)
C(6A) - Fe(1A) - C(4A) - C(5A)	-32.4(3)
C(7A) - Fe(1A) - C(4A) - C(5A)	-73.4(3)
C(2A) - Fe(1A) - C(4A) - C(9A)	-156.4(3)
C(3A) - Fe(1A) - C(4A) - C(9A)	82.3(9)
C(1A) - Fe(1A) - C(4A) - C(9A)	-58.2(3)
C(5A) - Fe(1A) - C(4A) - C(9A)	115.0(4)
C(6A) - Fe(1A) - C(4A) - C(9A)	82.6(3)
C(7A) - Fe(1A) - C(4A) - C(9A)	41.6(3)
C(9A) - C(4A) - C(5A) - C(6A)	-41.2(6)
Fe(1A) - C(4A) - C(5A) - C(6A)	56.0(3)
C(9A) - C(4A) - C(5A) - Fe(1A)	-97.2(4)
C(2A) - Fe(1A) - C(5A) - C(6A)	138.0(3)
C(3A) - Fe(1A) - C(5A) - C(6A)	42.0(3)
C(1A) - Fe(1A) - C(5A) - C(6A)	-119.0(3)
C(4A) - Fe(1A) - C(5A) - C(6A)	-128.1(4)
C(7A) - Fe(1A) - C(5A) - C(6A)	-33.0(2)
C(2A) - Fe(1A) - C(5A) - C(4A)	-93.9(3)
C(3A) - Fe(1A) - C(5A) - C(4A)	170.1(3)
C(1A) - Fe(1A) - C(5A) - C(4A)	9.2(4)
C(6A) - Fe(1A) - C(5A) - C(4A)	128.1(4)
C(7A) - Fe(1A) - C(5A) - C(4A)	95.1(3)
C(4A) - C(5A) - C(6A) - C(7A)	0.6(6)
Fe(1A) - C(5A) - C(6A) - C(7A)	57.8(4)
C(4A) - C(5A) - C(6A) - Fe(1A)	-57.2(4)

C(2A) - Fe(1A) - C(6A) - C(5A)	-51.0(3)
C(3A) - Fe(1A) - C(6A) - C(5A)	-147.8(3)
C(1A) - Fe(1A) - C(6A) - C(5A)	102.9(4)
C(4A) - Fe(1A) - C(6A) - C(5A)	32.3(2)
C(7A) - Fe(1A) - C(6A) - C(5A)	127.3(4)
C(2A) - Fe(1A) - C(6A) - C(7A)	-178.3(3)
C(3A) - Fe(1A) - C(6A) - C(7A)	84.9(3)
C(1A) - Fe(1A) - C(6A) - C(7A)	-24.4(4)
C(5A) - Fe(1A) - C(6A) - C(7A)	-127.3(4)
C(4A) - Fe(1A) - C(6A) - C(7A)	-95.1(3)
C(5A) - C(6A) - C(7A) - C(8A)	28.9(6)
Fe(1A) - C(6A) - C(7A) - C(8A)	85.3(4)
C(5A) - C(6A) - C(7A) - Fe(1A)	-56.4(3)
C(2A) - Fe(1A) - C(7A) - C(6A)	4.4(7)
C(3A) - Fe(1A) - C(7A) - C(6A)	-97.3(3)
C(1A) - Fe(1A) - C(7A) - C(6A)	163.7(3)
C(5A) - Fe(1A) - C(7A) - C(6A)	32.8(3)
C(4A) - Fe(1A) - C(7A) - C(6A)	73.3(3)
C(2A) - Fe(1A) - C(7A) - C(8A)	-117.9(6)
C(3A) - Fe(1A) - C(7A) - C(8A)	140.4(3)
C(1A) - Fe(1A) - C(7A) - C(8A)	41.4(3)
C(5A) - Fe(1A) - C(7A) - C(8A)	-89.5(3)
C(6A) - Fe(1A) - C(7A) - C(8A)	-122.3(4)
C(4A) - Fe(1A) - C(7A) - C(8A)	-49.0(3)
C(6A) - C(7A) - C(8A) - O(5A)	169.7(5)
Fe(1A) - C(7A) - C(8A) - O(5A)	-122.0(4)
C(6A) - C(7A) - C(8A) - C(9A)	-17.2(6)
Fe(1A) - C(7A) - C(8A) - C(9A)	51.2(4)
C(5A) - C(4A) - C(9A) - O(4A)	168.2(4)
Fe(1A) - C(4A) - C(9A) - O(4A)	94.8(3)
C(5A) - C(4A) - C(9A) - C(8A)	49.5(5)
Fe(1A) - C(4A) - C(9A) - C(8A)	-23.8(4)
C(5A) - C(4A) - C(9A) - C(10A)	-70.4(5)
Fe(1A) - C(4A) - C(9A) - C(10A)	-143.7(3)
O(5A) - C(8A) - C(9A) - O(4A)	36.1(5)
C(7A) - C(8A) - C(9A) - O(4A)	-137.6(4)
O(5A) - C(8A) - C(9A) - C(4A)	154.1(4)
C(7A) - C(8A) - C(9A) - C(4A)	-19.7(5)
O(5A) - C(8A) - C(9A) - C(10A)	-85.2(5)
C(7A) - C(8A) - C(9A) - C(10A)	101.0(4)
C(12A) - O(7A) - C(10A) - O(6A)	5.1(10)
C(12A) - O(7A) - C(10A) - C(9A)	-174.4(7)
C(11A) - O(6A) - C(10A) - O(7A)	2.2(10)
C(11A) - O(6A) - C(10A) - C(9A)	-178.3(8)
O(4A) - C(9A) - C(10A) - O(7A)	-169.7(4)
C(4A) - C(9A) - C(10A) - O(7A)	70.1(5)
C(8A) - C(9A) - C(10A) - O(7A)	-49.1(5)
O(4A) - C(9A) - C(10A) - O(6A)	10.7(5)
C(4A) - C(9A) - C(10A) - O(6A)	-109.5(4)
C(8A) - C(9A) - C(10A) - O(6A)	131.4(4)
C(3B) - Fe(1B) - C(1B) - O(1B)	-135(12)
C(2B) - Fe(1B) - C(1B) - O(1B)	131(12)
C(6B) - Fe(1B) - C(1B) - O(1B)	-28(13)
C(5B) - Fe(1B) - C(1B) - O(1B)	30(13)
C(4B) - Fe(1B) - C(1B) - O(1B)	37(12)
C(7B) - Fe(1B) - C(1B) - O(1B)	-42(13)
C(3B) - Fe(1B) - C(2B) - O(2B)	173(100)
C(1B) - Fe(1B) - C(2B) - O(2B)	-88(26)
C(6B) - Fe(1B) - C(2B) - O(2B)	75(26)
C(5B) - Fe(1B) - C(2B) - O(2B)	46(26)
C(4B) - Fe(1B) - C(2B) - O(2B)	7(26)
C(7B) - Fe(1B) - C(2B) - O(2B)	69(26)
C(2B) - Fe(1B) - C(3B) - O(3B)	-164(100)
C(1B) - Fe(1B) - C(3B) - O(3B)	99(26)
C(6B) - Fe(1B) - C(3B) - O(3B)	-41(26)
C(5B) - Fe(1B) - C(3B) - O(3B)	-67(26)
C(4B) - Fe(1B) - C(3B) - O(3B)	-47(26)
C(7B) - Fe(1B) - C(3B) - O(3B)	-1(26)
C(3B) - Fe(1B) - C(4B) - C(5B)	-25.9(9)
C(2B) - Fe(1B) - C(4B) - C(5B)	90.6(3)
C(1B) - Fe(1B) - C(4B) - C(5B)	-172.4(3)

C(6B) - Fe(1B) - C(4B) - C(5B)	-32.9(3)
C(7B) - Fe(1B) - C(4B) - C(5B)	-73.7(3)
C(3B) - Fe(1B) - C(4B) - C(9B)	89.7(8)
C(2B) - Fe(1B) - C(4B) - C(9B)	-153.8(3)
C(1B) - Fe(1B) - C(4B) - C(9B)	-56.8(3)
C(6B) - Fe(1B) - C(4B) - C(9B)	82.7(3)
C(5B) - Fe(1B) - C(4B) - C(9B)	115.6(4)
C(7B) - Fe(1B) - C(4B) - C(9B)	41.8(3)
C(9B) - C(4B) - C(5B) - C(6B)	-41.9(6)
Fe(1B) - C(4B) - C(5B) - C(6B)	55.9(3)
C(9B) - C(4B) - C(5B) - Fe(1B)	-97.8(4)
C(3B) - Fe(1B) - C(5B) - C(4B)	172.0(3)
C(2B) - Fe(1B) - C(5B) - C(4B)	-91.9(3)
C(1B) - Fe(1B) - C(5B) - C(4B)	10.3(4)
C(6B) - Fe(1B) - C(5B) - C(4B)	127.6(4)
C(7B) - Fe(1B) - C(5B) - C(4B)	95.1(3)
C(3B) - Fe(1B) - C(5B) - C(6B)	44.4(3)
C(2B) - Fe(1B) - C(5B) - C(6B)	140.5(3)
C(1B) - Fe(1B) - C(5B) - C(6B)	-117.3(3)
C(4B) - Fe(1B) - C(5B) - C(6B)	-127.6(4)
C(7B) - Fe(1B) - C(5B) - C(6B)	-32.5(3)
C(4B) - C(5B) - C(6B) - C(7B)	0.3(6)
Fe(1B) - C(5B) - C(6B) - C(7B)	57.3(4)
C(4B) - C(5B) - C(6B) - Fe(1B)	-57.1(4)
C(3B) - Fe(1B) - C(6B) - C(5B)	-145.9(3)
C(2B) - Fe(1B) - C(6B) - C(5B)	-49.0(3)
C(1B) - Fe(1B) - C(6B) - C(5B)	105.4(4)
C(4B) - Fe(1B) - C(6B) - C(5B)	32.3(2)
C(7B) - Fe(1B) - C(6B) - C(5B)	128.0(4)
C(3B) - Fe(1B) - C(6B) - C(7B)	86.1(3)
C(2B) - Fe(1B) - C(6B) - C(7B)	-177.0(3)
C(1B) - Fe(1B) - C(6B) - C(7B)	-22.6(4)
C(5B) - Fe(1B) - C(6B) - C(7B)	-128.0(4)
C(4B) - Fe(1B) - C(6B) - C(7B)	-95.7(3)
C(5B) - C(6B) - C(7B) - C(8B)	29.7(6)
Fe(1B) - C(6B) - C(7B) - C(8B)	85.7(4)
C(5B) - C(6B) - C(7B) - Fe(1B)	-56.0(3)
C(3B) - Fe(1B) - C(7B) - C(6B)	-96.4(3)
C(2B) - Fe(1B) - C(7B) - C(6B)	8.4(8)
C(1B) - Fe(1B) - C(7B) - C(6B)	164.7(3)
C(5B) - Fe(1B) - C(7B) - C(6B)	32.5(3)
C(4B) - Fe(1B) - C(7B) - C(6B)	72.7(3)
C(3B) - Fe(1B) - C(7B) - C(8B)	142.8(3)
C(2B) - Fe(1B) - C(7B) - C(8B)	-112.4(7)
C(1B) - Fe(1B) - C(7B) - C(8B)	43.8(3)
C(6B) - Fe(1B) - C(7B) - C(8B)	-120.9(4)
C(5B) - Fe(1B) - C(7B) - C(8B)	-88.4(3)
C(4B) - Fe(1B) - C(7B) - C(8B)	-48.2(3)
C(6B) - C(7B) - C(8B) - O(5B)	168.6(4)
Fe(1B) - C(7B) - C(8B) - O(5B)	-123.0(4)
C(6B) - C(7B) - C(8B) - C(9B)	-18.1(6)
Fe(1B) - C(7B) - C(8B) - C(9B)	50.3(4)
C(5B) - C(4B) - C(9B) - O(4B)	168.6(4)
Fe(1B) - C(4B) - C(9B) - O(4B)	94.2(3)
C(5B) - C(4B) - C(9B) - C(10B)	-70.1(5)
Fe(1B) - C(4B) - C(9B) - C(10B)	-144.5(3)
C(5B) - C(4B) - C(9B) - C(8B)	50.1(5)
Fe(1B) - C(4B) - C(9B) - C(8B)	-24.3(4)
O(5B) - C(8B) - C(9B) - O(4B)	36.8(5)
C(7B) - C(8B) - C(9B) - O(4B)	-136.9(4)
O(5B) - C(8B) - C(9B) - C(4B)	154.8(4)
C(7B) - C(8B) - C(9B) - C(4B)	-18.9(5)
O(5B) - C(8B) - C(9B) - C(10B)	-84.3(5)
C(7B) - C(8B) - C(9B) - C(10B)	102.0(4)
C(11B) - O(6B) - C(10B) - O(7B)	2.0(10)
C(11B) - O(6B) - C(10B) - C(9B)	-177.9(7)
C(12B) - O(7B) - C(10B) - O(6B)	4.3(10)
C(12B) - O(7B) - C(10B) - C(9B)	-175.7(7)
O(4B) - C(9B) - C(10B) - O(6B)	10.6(5)
C(4B) - C(9B) - C(10B) - O(6B)	-109.8(4)
C(8B) - C(9B) - C(10B) - O(6B)	131.3(4)

O(4B) - C(9B) - C(10B) - O(7B)	-169.4(4)
C(4B) - C(9B) - C(10B) - O(7B)	70.3(5)
C(8B) - C(9B) - C(10B) - O(7B)	-48.7(5)
C(2C) - Fe(1C) - C(1C) - O(1C)	-159(100)
C(3C) - Fe(1C) - C(1C) - O(1C)	-65(27)
C(5C) - Fe(1C) - C(1C) - O(1C)	101(27)
C(6C) - Fe(1C) - C(1C) - O(1C)	43(27)
C(4C) - Fe(1C) - C(1C) - O(1C)	107(27)
C(7C) - Fe(1C) - C(1C) - O(1C)	28(27)
C(3C) - Fe(1C) - C(2C) - O(2C)	-129(25)
C(1C) - Fe(1C) - C(2C) - O(2C)	-29(25)
C(5C) - Fe(1C) - C(2C) - O(2C)	104(25)
C(6C) - Fe(1C) - C(2C) - O(2C)	133(25)
C(4C) - Fe(1C) - C(2C) - O(2C)	64(25)
C(7C) - Fe(1C) - C(2C) - O(2C)	127(24)
C(2C) - Fe(1C) - C(3C) - O(3C)	-180(100)
C(1C) - Fe(1C) - C(3C) - O(3C)	82(25)
C(5C) - Fe(1C) - C(3C) - O(3C)	-84(25)
C(6C) - Fe(1C) - C(3C) - O(3C)	-57(25)
C(4C) - Fe(1C) - C(3C) - O(3C)	-65(25)
C(7C) - Fe(1C) - C(3C) - O(3C)	-17(25)
C(2C) - Fe(1C) - C(4C) - C(5C)	90.2(3)
C(3C) - Fe(1C) - C(4C) - C(5C)	-25.0(9)
C(1C) - Fe(1C) - C(4C) - C(5C)	-172.2(3)
C(6C) - Fe(1C) - C(4C) - C(5C)	-32.8(3)
C(7C) - Fe(1C) - C(4C) - C(5C)	-73.7(3)
C(2C) - Fe(1C) - C(4C) - C(9C)	-154.5(3)
C(3C) - Fe(1C) - C(4C) - C(9C)	90.2(8)
C(1C) - Fe(1C) - C(4C) - C(9C)	-57.0(3)
C(5C) - Fe(1C) - C(4C) - C(9C)	115.3(4)
C(6C) - Fe(1C) - C(4C) - C(9C)	82.4(3)
C(7C) - Fe(1C) - C(4C) - C(9C)	41.6(3)
C(9C) - C(4C) - C(5C) - C(6C)	-42.1(6)
Fe(1C) - C(4C) - C(5C) - C(6C)	56.1(3)
C(9C) - C(4C) - C(5C) - Fe(1C)	-98.1(4)
C(2C) - Fe(1C) - C(5C) - C(4C)	-92.1(3)
C(3C) - Fe(1C) - C(5C) - C(4C)	172.2(3)
C(1C) - Fe(1C) - C(5C) - C(4C)	10.5(4)
C(6C) - Fe(1C) - C(5C) - C(4C)	127.7(4)
C(7C) - Fe(1C) - C(5C) - C(4C)	95.2(3)
C(2C) - Fe(1C) - C(5C) - C(6C)	140.2(3)
C(3C) - Fe(1C) - C(5C) - C(6C)	44.5(4)
C(1C) - Fe(1C) - C(5C) - C(6C)	-117.2(3)
C(4C) - Fe(1C) - C(5C) - C(6C)	-127.7(4)
C(7C) - Fe(1C) - C(5C) - C(6C)	-32.5(3)
C(4C) - C(5C) - C(6C) - C(7C)	0.2(6)
Fe(1C) - C(5C) - C(6C) - C(7C)	57.2(4)
C(4C) - C(5C) - C(6C) - Fe(1C)	-57.0(4)
C(2C) - Fe(1C) - C(6C) - C(5C)	-49.1(3)
C(3C) - Fe(1C) - C(6C) - C(5C)	-145.6(3)
C(1C) - Fe(1C) - C(6C) - C(5C)	104.8(4)
C(4C) - Fe(1C) - C(6C) - C(5C)	32.4(3)
C(7C) - Fe(1C) - C(6C) - C(5C)	127.9(4)
C(2C) - Fe(1C) - C(6C) - C(7C)	-177.0(3)
C(3C) - Fe(1C) - C(6C) - C(7C)	86.4(3)
C(1C) - Fe(1C) - C(6C) - C(7C)	-23.1(4)
C(5C) - Fe(1C) - C(6C) - C(7C)	-127.9(4)
C(4C) - Fe(1C) - C(6C) - C(7C)	-95.6(3)
C(5C) - C(6C) - C(7C) - C(8C)	29.4(6)
Fe(1C) - C(6C) - C(7C) - C(8C)	85.1(4)
C(5C) - C(6C) - C(7C) - Fe(1C)	-55.7(3)
C(2C) - Fe(1C) - C(7C) - C(8C)	-112.9(6)
C(3C) - Fe(1C) - C(7C) - C(8C)	143.0(3)
C(1C) - Fe(1C) - C(7C) - C(8C)	43.2(3)
C(5C) - Fe(1C) - C(7C) - C(8C)	-88.5(3)
C(6C) - Fe(1C) - C(7C) - C(8C)	-121.1(4)
C(4C) - Fe(1C) - C(7C) - C(8C)	-48.2(3)
C(2C) - Fe(1C) - C(7C) - C(6C)	8.2(8)
C(3C) - Fe(1C) - C(7C) - C(6C)	-95.9(3)
C(1C) - Fe(1C) - C(7C) - C(6C)	164.3(3)
C(5C) - Fe(1C) - C(7C) - C(6C)	32.6(3)

C(4C) - Fe(1C) - C(7C) - C(6C)	72.9(3)
C(6C) - C(7C) - C(8C) - O(5C)	168.0(4)
Fe(1C) - C(7C) - C(8C) - O(5C)	-123.8(4)
C(6C) - C(7C) - C(8C) - C(9C)	-17.3(6)
Fe(1C) - C(7C) - C(8C) - C(9C)	50.8(4)
C(5C) - C(4C) - C(9C) - O(4C)	168.3(4)
Fe(1C) - C(4C) - C(9C) - O(4C)	93.9(3)
C(5C) - C(4C) - C(9C) - C(10C)	-69.3(5)
Fe(1C) - C(4C) - C(9C) - C(10C)	-143.7(3)
C(5C) - C(4C) - C(9C) - C(8C)	50.5(5)
Fe(1C) - C(4C) - C(9C) - C(8C)	-23.9(4)
O(5C) - C(8C) - C(9C) - O(4C)	38.0(5)
C(7C) - C(8C) - C(9C) - O(4C)	-137.0(4)
O(5C) - C(8C) - C(9C) - C(4C)	155.2(4)
C(7C) - C(8C) - C(9C) - C(4C)	-19.8(5)
O(5C) - C(8C) - C(9C) - C(10C)	-84.0(5)
C(7C) - C(8C) - C(9C) - C(10C)	100.9(4)
C(12C) - O(7C) - C(10C) - O(6C)	6.4(10)
C(12C) - O(7C) - C(10C) - C(9C)	-174.4(8)
C(11C) - O(6C) - C(10C) - O(7C)	0.2(10)
C(11C) - O(6C) - C(10C) - C(9C)	-179.0(8)
O(4C) - C(9C) - C(10C) - O(7C)	-169.2(4)
C(4C) - C(9C) - C(10C) - O(7C)	69.9(5)
C(8C) - C(9C) - C(10C) - O(7C)	-48.3(5)
O(4C) - C(9C) - C(10C) - O(6C)	10.0(5)
C(4C) - C(9C) - C(10C) - O(6C)	-110.9(4)
C(8C) - C(9C) - C(10C) - O(6C)	131.0(4)
C(2D) - Fe(1D) - C(1D) - O(1D)	138(17)
C(3D) - Fe(1D) - C(1D) - O(1D)	-127(17)
C(5D) - Fe(1D) - C(1D) - O(1D)	38(17)
C(6D) - Fe(1D) - C(1D) - O(1D)	-19(17)
C(4D) - Fe(1D) - C(1D) - O(1D)	43(17)
C(7D) - Fe(1D) - C(1D) - O(1D)	-35(17)
C(3D) - Fe(1D) - C(2D) - O(2D)	65(54)
C(1D) - Fe(1D) - C(2D) - O(2D)	164(100)
C(5D) - Fe(1D) - C(2D) - O(2D)	-63(54)
C(6D) - Fe(1D) - C(2D) - O(2D)	-34(54)
C(4D) - Fe(1D) - C(2D) - O(2D)	-103(100)
C(7D) - Fe(1D) - C(2D) - O(2D)	-38(54)
C(2D) - Fe(1D) - C(3D) - O(3D)	133(24)
C(1D) - Fe(1D) - C(3D) - O(3D)	34(24)
C(5D) - Fe(1D) - C(3D) - O(3D)	-131(24)
C(6D) - Fe(1D) - C(3D) - O(3D)	-106(24)
C(4D) - Fe(1D) - C(3D) - O(3D)	-105(24)
C(7D) - Fe(1D) - C(3D) - O(3D)	-66(24)
C(2D) - Fe(1D) - C(4D) - C(5D)	88.8(3)
C(3D) - Fe(1D) - C(4D) - C(5D)	-33.5(9)
C(1D) - Fe(1D) - C(4D) - C(5D)	-173.1(3)
C(6D) - Fe(1D) - C(4D) - C(5D)	-32.4(3)
C(7D) - Fe(1D) - C(4D) - C(5D)	-73.5(3)
C(2D) - Fe(1D) - C(4D) - C(9D)	-156.3(3)
C(3D) - Fe(1D) - C(4D) - C(9D)	81.4(9)
C(1D) - Fe(1D) - C(4D) - C(9D)	-58.2(3)
C(5D) - Fe(1D) - C(4D) - C(9D)	115.0(4)
C(6D) - Fe(1D) - C(4D) - C(9D)	82.6(3)
C(7D) - Fe(1D) - C(4D) - C(9D)	41.4(3)
C(9D) - C(4D) - C(5D) - C(6D)	-41.5(6)
Fe(1D) - C(4D) - C(5D) - C(6D)	56.3(4)
C(9D) - C(4D) - C(5D) - Fe(1D)	-97.8(4)
C(2D) - Fe(1D) - C(5D) - C(6D)	138.5(3)
C(3D) - Fe(1D) - C(5D) - C(6D)	42.0(4)
C(1D) - Fe(1D) - C(5D) - C(6D)	-118.7(3)
C(4D) - Fe(1D) - C(5D) - C(6D)	-127.9(4)
C(7D) - Fe(1D) - C(5D) - C(6D)	-32.9(3)
C(2D) - Fe(1D) - C(5D) - C(4D)	-93.6(3)
C(3D) - Fe(1D) - C(5D) - C(4D)	169.9(3)
C(1D) - Fe(1D) - C(5D) - C(4D)	9.3(4)
C(6D) - Fe(1D) - C(5D) - C(4D)	127.9(4)
C(7D) - Fe(1D) - C(5D) - C(4D)	95.1(3)
C(4D) - C(5D) - C(6D) - C(7D)	-0.4(6)
Fe(1D) - C(5D) - C(6D) - C(7D)	57.0(4)

C(4D) - C(5D) - C(6D) - Fe(1D)	-57.3(4)
C(2D) - Fe(1D) - C(6D) - C(5D)	-50.3(4)
C(3D) - Fe(1D) - C(6D) - C(5D)	-147.8(3)
C(1D) - Fe(1D) - C(6D) - C(5D)	103.4(4)
C(4D) - Fe(1D) - C(6D) - C(5D)	32.5(3)
C(7D) - Fe(1D) - C(6D) - C(5D)	127.8(4)
C(2D) - Fe(1D) - C(6D) - C(7D)	-178.1(3)
C(3D) - Fe(1D) - C(6D) - C(7D)	84.4(3)
C(1D) - Fe(1D) - C(6D) - C(7D)	-24.4(4)
C(5D) - Fe(1D) - C(6D) - C(7D)	-127.8(4)
C(4D) - Fe(1D) - C(6D) - C(7D)	-95.3(3)
C(5D) - C(6D) - C(7D) - C(8D)	30.6(6)
Fe(1D) - C(6D) - C(7D) - C(8D)	86.4(4)
C(5D) - C(6D) - C(7D) - Fe(1D)	-55.9(4)
C(2D) - Fe(1D) - C(7D) - C(8D)	-116.7(6)
C(3D) - Fe(1D) - C(7D) - C(8D)	140.5(3)
C(1D) - Fe(1D) - C(7D) - C(8D)	42.0(3)
C(5D) - Fe(1D) - C(7D) - C(8D)	-89.3(3)
C(6D) - Fe(1D) - C(7D) - C(8D)	-121.7(4)
C(4D) - Fe(1D) - C(7D) - C(8D)	-48.8(3)
C(2D) - Fe(1D) - C(7D) - C(6D)	4.9(7)
C(3D) - Fe(1D) - C(7D) - C(6D)	-97.8(3)
C(1D) - Fe(1D) - C(7D) - C(6D)	163.7(3)
C(5D) - Fe(1D) - C(7D) - C(6D)	32.3(3)
C(4D) - Fe(1D) - C(7D) - C(6D)	72.9(3)
C(6D) - C(7D) - C(8D) - O(5D)	168.7(4)
Fe(1D) - C(7D) - C(8D) - O(5D)	-122.2(4)
C(6D) - C(7D) - C(8D) - C(9D)	-18.2(6)
Fe(1D) - C(7D) - C(8D) - C(9D)	51.0(4)
C(5D) - C(4D) - C(9D) - O(4D)	167.7(4)
Fe(1D) - C(4D) - C(9D) - O(4D)	94.0(3)
C(5D) - C(4D) - C(9D) - C(10D)	-70.2(5)
Fe(1D) - C(4D) - C(9D) - C(10D)	-143.9(3)
C(5D) - C(4D) - C(9D) - C(8D)	50.1(5)
Fe(1D) - C(4D) - C(9D) - C(8D)	-23.6(4)
O(5D) - C(8D) - C(9D) - O(4D)	37.0(5)
C(7D) - C(8D) - C(9D) - O(4D)	-136.7(4)
O(5D) - C(8D) - C(9D) - C(4D)	154.2(4)
C(7D) - C(8D) - C(9D) - C(4D)	-19.5(5)
O(5D) - C(8D) - C(9D) - C(10D)	-84.7(4)
C(7D) - C(8D) - C(9D) - C(10D)	101.6(4)
C(11D) - O(6D) - C(10D) - O(7D)	-0.3(11)
C(11D) - O(6D) - C(10D) - C(9D)	-179.6(8)
C(12D) - O(7D) - C(10D) - O(6D)	6.8(10)
C(12D) - O(7D) - C(10D) - C(9D)	-173.9(7)
O(4D) - C(9D) - C(10D) - O(6D)	9.9(5)
C(4D) - C(9D) - C(10D) - O(6D)	-110.8(4)
C(8D) - C(9D) - C(10D) - O(6D)	130.5(4)
O(4D) - C(9D) - C(10D) - O(7D)	-169.4(4)
C(4D) - C(9D) - C(10D) - O(7D)	69.9(5)
C(8D) - C(9D) - C(10D) - O(7D)	-48.8(5)
C(2E) - Fe(1E) - C(1E) - O(2E)	173(100)
C(3E) - Fe(1E) - C(1E) - O(2E)	-92(18)
C(6E) - Fe(1E) - C(1E) - O(2E)	15(19)
C(5E) - Fe(1E) - C(1E) - O(2E)	72(19)
C(4E) - Fe(1E) - C(1E) - O(2E)	78(18)
C(7E) - Fe(1E) - C(1E) - O(2E)	0(19)
C(3E) - Fe(1E) - C(2E) - O(3E)	176(100)
C(1E) - Fe(1E) - C(2E) - O(3E)	-85(61)
C(6E) - Fe(1E) - C(2E) - O(3E)	78(61)
C(5E) - Fe(1E) - C(2E) - O(3E)	48(61)
C(4E) - Fe(1E) - C(2E) - O(3E)	9(61)
C(7E) - Fe(1E) - C(2E) - O(3E)	76(61)
C(2E) - Fe(1E) - C(3E) - O(4E)	134(20)
C(1E) - Fe(1E) - C(3E) - O(4E)	35(20)
C(6E) - Fe(1E) - C(3E) - O(4E)	-105(20)
C(5E) - Fe(1E) - C(3E) - O(4E)	-130(20)
C(4E) - Fe(1E) - C(3E) - O(4E)	-104(20)
C(7E) - Fe(1E) - C(3E) - O(4E)	-65(20)
C(2E) - Fe(1E) - C(4E) - C(5E)	88.6(3)
C(3E) - Fe(1E) - C(4E) - C(5E)	-33.4(9)

C(1E) - Fe(1E) - C(4E) - C(5E)	-172.9(3)
C(6E) - Fe(1E) - C(4E) - C(5E)	-32.4(3)
C(7E) - Fe(1E) - C(4E) - C(5E)	-73.2(3)
C(2E) - Fe(1E) - C(4E) - C(9E)	-156.5(3)
C(3E) - Fe(1E) - C(4E) - C(9E)	81.5(8)
C(1E) - Fe(1E) - C(4E) - C(9E)	-58.1(3)
C(6E) - Fe(1E) - C(4E) - C(9E)	82.5(3)
C(5E) - Fe(1E) - C(4E) - C(9E)	114.9(4)
C(7E) - Fe(1E) - C(4E) - C(9E)	41.7(3)
C(9E) - C(4E) - C(5E) - C(6E)	-42.7(6)
Fe(1E) - C(4E) - C(5E) - C(6E)	55.4(4)
C(9E) - C(4E) - C(5E) - Fe(1E)	-98.1(4)
C(2E) - Fe(1E) - C(5E) - C(6E)	137.9(3)
C(3E) - Fe(1E) - C(5E) - C(6E)	41.8(4)
C(1E) - Fe(1E) - C(5E) - C(6E)	-118.6(3)
C(4E) - Fe(1E) - C(5E) - C(6E)	-128.1(4)
C(7E) - Fe(1E) - C(5E) - C(6E)	-32.8(3)
C(2E) - Fe(1E) - C(5E) - C(4E)	-94.0(3)
C(3E) - Fe(1E) - C(5E) - C(4E)	169.9(3)
C(1E) - Fe(1E) - C(5E) - C(4E)	9.5(4)
C(6E) - Fe(1E) - C(5E) - C(4E)	128.1(4)
C(7E) - Fe(1E) - C(5E) - C(4E)	95.3(3)
C(4E) - C(5E) - C(6E) - C(7E)	1.4(6)
Fe(1E) - C(5E) - C(6E) - C(7E)	57.6(4)
C(4E) - C(5E) - C(6E) - Fe(1E)	-56.3(4)
C(2E) - Fe(1E) - C(6E) - C(5E)	-51.1(4)
C(3E) - Fe(1E) - C(6E) - C(5E)	-148.0(3)
C(1E) - Fe(1E) - C(6E) - C(5E)	103.4(4)
C(4E) - Fe(1E) - C(6E) - C(5E)	32.3(3)
C(7E) - Fe(1E) - C(6E) - C(5E)	127.4(4)
C(2E) - Fe(1E) - C(6E) - C(7E)	-178.6(3)
C(3E) - Fe(1E) - C(6E) - C(7E)	84.6(3)
C(1E) - Fe(1E) - C(6E) - C(7E)	-24.0(4)
C(5E) - Fe(1E) - C(6E) - C(7E)	-127.4(4)
C(4E) - Fe(1E) - C(6E) - C(7E)	-95.2(3)
C(5E) - C(6E) - C(7E) - C(8E)	28.9(6)
Fe(1E) - C(6E) - C(7E) - C(8E)	85.4(4)
C(5E) - C(6E) - C(7E) - Fe(1E)	-56.5(4)
C(2E) - Fe(1E) - C(7E) - C(6E)	3.7(8)
C(3E) - Fe(1E) - C(7E) - C(6E)	-97.4(3)
C(1E) - Fe(1E) - C(7E) - C(6E)	163.9(3)
C(5E) - Fe(1E) - C(7E) - C(6E)	32.7(3)
C(4E) - Fe(1E) - C(7E) - C(6E)	73.3(3)
C(2E) - Fe(1E) - C(7E) - C(8E)	-118.0(6)
C(3E) - Fe(1E) - C(7E) - C(8E)	140.8(3)
C(1E) - Fe(1E) - C(7E) - C(8E)	42.2(3)
C(6E) - Fe(1E) - C(7E) - C(8E)	-121.7(4)
C(5E) - Fe(1E) - C(7E) - C(8E)	-89.0(3)
C(4E) - Fe(1E) - C(7E) - C(8E)	-48.4(3)
C(6E) - C(7E) - C(8E) - O(6E)	168.7(4)
Fe(1E) - C(7E) - C(8E) - O(6E)	-122.7(4)
C(6E) - C(7E) - C(8E) - C(9E)	-17.6(6)
Fe(1E) - C(7E) - C(8E) - C(9E)	51.1(4)
C(5E) - C(4E) - C(9E) - O(5E)	169.2(4)
Fe(1E) - C(4E) - C(9E) - O(5E)	94.7(3)
C(5E) - C(4E) - C(9E) - C(8E)	50.6(5)
Fe(1E) - C(4E) - C(9E) - C(8E)	-23.9(4)
C(5E) - C(4E) - C(9E) - C(10E)	-69.5(5)
Fe(1E) - C(4E) - C(9E) - C(10E)	-144.0(3)
O(6E) - C(8E) - C(9E) - O(5E)	36.6(5)
C(7E) - C(8E) - C(9E) - O(5E)	-137.6(4)
O(6E) - C(8E) - C(9E) - C(4E)	154.5(4)
C(7E) - C(8E) - C(9E) - C(4E)	-19.7(5)
O(6E) - C(8E) - C(9E) - C(10E)	-84.9(5)
C(7E) - C(8E) - C(9E) - C(10E)	100.9(4)
C(12E) - O(8E) - C(10E) - O(7E)	4.1(10)
C(12E) - O(8E) - C(10E) - C(9E)	-176.4(7)
C(11E) - O(7E) - C(10E) - O(8E)	3.0(11)
C(11E) - O(7E) - C(10E) - C(9E)	-176.5(8)
O(5E) - C(9E) - C(10E) - O(8E)	-169.9(4)
C(4E) - C(9E) - C(10E) - O(8E)	69.9(5)

C(8E) - C(9E) - C(10E) - O(8E)	-48.8(5)
O(5E) - C(9E) - C(10E) - O(7E)	9.7(5)
C(4E) - C(9E) - C(10E) - O(7E)	-110.5(4)
C(8E) - C(9E) - C(10E) - O(7E)	130.8(4)

Symmetry transformations used to generate equivalent atoms:

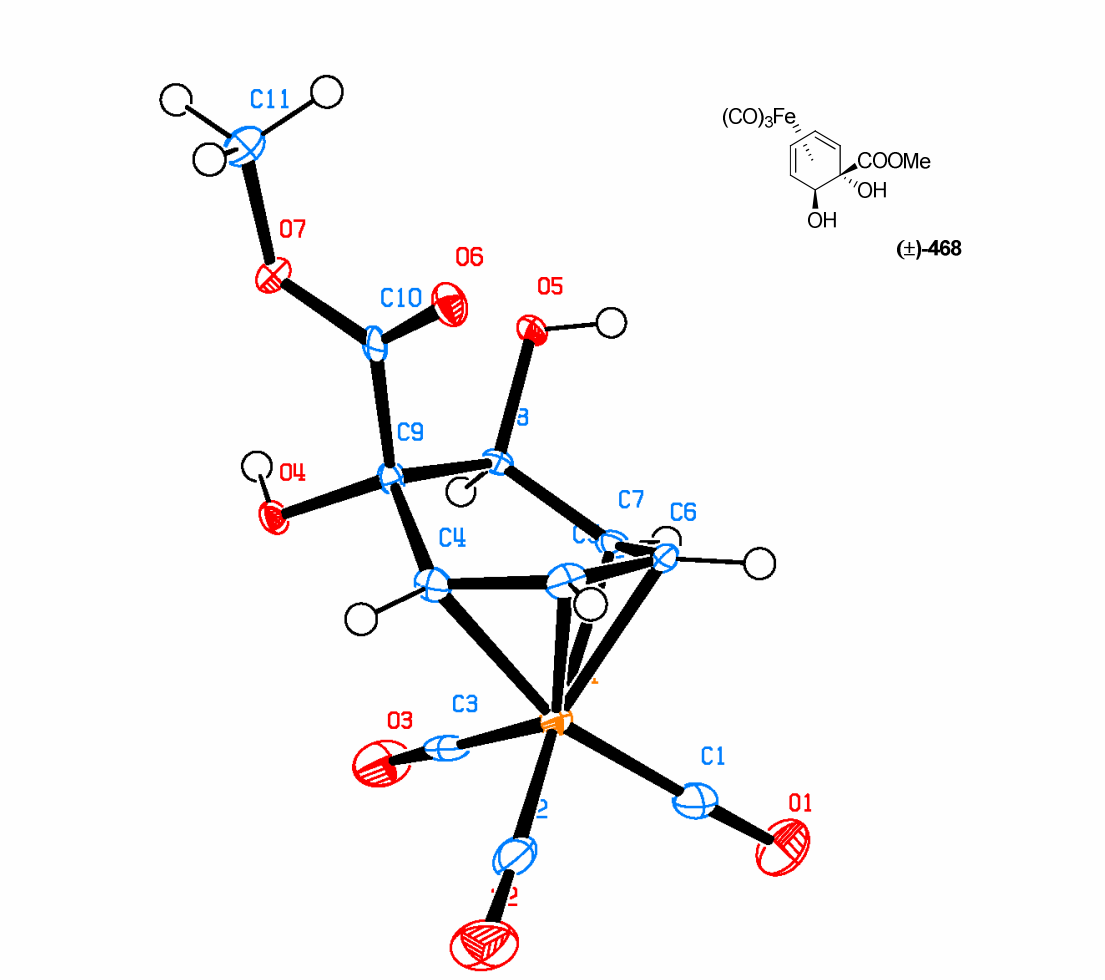


Figure 29 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **(±)-468**

Table 24 Crystal data and structure refinement (±)-468

Identification code	p09sel4
Empirical formula	C11 H10 Fe O7
Formula weight	310.04
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	P-1
Unit cell dimensions	a = 6.9380(2)Å α = 99.162(3)°
	b = 7.4496(3)Å β = 99.099(3)°
	c = 12.0918(4)Å γ = 95.993(3)°
Volume	603.82(4) $Å^3$
Z	2
Density (calculated)	1.705 Mg/m^3
Absorption coefficient	1.275 mm^{-1}
F(000)	316
Crystal size	0.14 x 0.09 x 0.02 mm
Theta range for data collection	3.00 to 25.01°
Index ranges	-8<=h<=8; -8<=k<=8; -14<=l<=14
Reflections collected	8848
Independent reflections	2129 [R(int) = 0.0716]
Reflections observed (>2σ)	1672
Data Completeness	0.999
Absorption correction	Analytical
Max. and min. transmission	0.835 and 0.494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2129 / 10 / 193
Goodness-of-fit on F^2	0.926
Final R indices [I>2σ(I)]	R1 = 0.0292 wR2 = 0.0579
R indices (all data)	R1 = 0.0449 wR2 = 0.0604
Largest diff. peak and hole	0.356 and -0.318 $eÅ^{-3}$

Notes:

Crystal quality was moderate, and given the diffracting ability of the sample, data were truncated to a max Bragg angle of 25°.

H4-H7 were located and refined at a distance of 0.98Å from the relevant parent atoms.

Hydrogen bonding gives rise to 1-D polymers in the lattice.

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O4-H4A	0.840	1.977	178.01	2.816	O5 [-x+1, -y+2, -z+2]
O5-H5A	0.840	1.979	173.31	2.815	O6 [-x+2, -y+2, -z+2]

Table 25 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) (±)-468. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	7218(1)	6250(1)	6939(1)	12(1)

O(1)	8505(3)	7524(3)	4965(2)	43(1)
O(2)	7213(3)	2338(3)	6067(2)	38(1)
O(3)	3025(3)	6622(3)	6449(2)	32(1)
O(4)	4317(2)	6642(2)	9191(1)	12(1)
O(5)	7573(2)	10556(2)	9764(1)	12(1)
O(6)	9165(2)	7467(2)	10819(1)	15(1)
O(7)	6212(2)	7797(2)	11281(1)	13(1)
C(1)	7993(4)	7008(4)	5720(2)	22(1)
C(2)	7218(4)	3875(4)	6386(2)	20(1)
C(3)	4665(4)	6451(3)	6641(2)	18(1)
C(4)	7224(3)	5759(3)	8601(2)	12(1)
C(5)	9161(3)	6156(3)	8389(2)	13(1)
C(6)	9564(3)	7831(3)	8031(2)	13(1)
C(7)	7951(3)	8851(3)	7927(2)	12(1)
C(8)	6705(3)	9067(3)	8847(2)	9(1)
C(9)	6358(3)	7228(3)	9296(2)	9(1)
C(10)	7417(3)	7505(3)	10544(2)	10(1)
C(11)	7085(4)	7964(4)	12472(2)	19(1)

Table 26 Bond lengths [Å] and angles [°] for (±)-468

Fe(1)-C(3)	1.778(3)	Fe(1)-C(2)	1.789(3)
Fe(1)-C(1)	1.798(3)	Fe(1)-C(6)	2.051(2)
Fe(1)-C(5)	2.051(2)	Fe(1)-C(7)	2.075(2)
Fe(1)-C(4)	2.098(2)	O(1)-C(1)	1.137(3)
O(2)-C(2)	1.148(3)	O(3)-C(3)	1.149(3)
O(4)-C(9)	1.416(3)	O(4)-H(4A)	0.8400
O(5)-C(8)	1.443(3)	O(5)-H(5A)	0.8400
O(6)-C(10)	1.210(3)	O(7)-C(10)	1.323(3)
O(7)-C(11)	1.452(3)	C(4)-C(5)	1.417(3)
C(4)-C(9)	1.506(3)	C(4)-H(4)	0.977(5)
C(5)-C(6)	1.400(3)	C(5)-H(5)	0.978(5)
C(6)-C(7)	1.417(3)	C(6)-H(6)	0.978(5)
C(7)-C(8)	1.512(3)	C(7)-H(7)	0.979(5)
C(8)-C(9)	1.562(3)	C(8)-H(8)	1.0000
C(9)-C(10)	1.542(3)	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(3)-Fe(1)-C(2)	101.33(11)	C(3)-Fe(1)-C(1)	99.99(11)
C(2)-Fe(1)-C(1)	93.81(12)	C(3)-Fe(1)-C(6)	133.09(10)
C(2)-Fe(1)-C(6)	122.98(11)	C(1)-Fe(1)-C(6)	92.24(11)
C(3)-Fe(1)-C(5)	134.19(10)	C(2)-Fe(1)-C(5)	92.66(10)
C(1)-Fe(1)-C(5)	122.55(11)	C(6)-Fe(1)-C(5)	39.91(10)
C(3)-Fe(1)-C(7)	93.79(10)	C(2)-Fe(1)-C(7)	162.29(10)
C(1)-Fe(1)-C(7)	92.57(11)	C(6)-Fe(1)-C(7)	40.17(9)
C(5)-Fe(1)-C(7)	70.04(9)	C(3)-Fe(1)-C(4)	95.54(10)
C(2)-Fe(1)-C(4)	92.56(10)	C(1)-Fe(1)-C(4)	161.71(10)
C(6)-Fe(1)-C(4)	69.97(9)	C(5)-Fe(1)-C(4)	39.92(9)
C(7)-Fe(1)-C(4)	76.72(9)	C(9)-O(4)-H(4A)	109.5
C(8)-O(5)-H(5A)	109.5	C(10)-O(7)-C(11)	115.90(18)
O(1)-C(1)-Fe(1)	178.4(3)	O(2)-C(2)-Fe(1)	177.7(2)
O(3)-C(3)-Fe(1)	178.5(2)	C(5)-C(4)-C(9)	118.9(2)
C(5)-C(4)-Fe(1)	68.24(13)	C(9)-C(4)-Fe(1)	111.38(15)
C(5)-C(4)-H(4)	116.4(14)	C(9)-C(4)-H(4)	115.6(14)
Fe(1)-C(4)-H(4)	117.8(15)	C(6)-C(5)-C(4)	115.3(2)
C(6)-C(5)-Fe(1)	70.02(13)	C(4)-C(5)-Fe(1)	71.84(13)
C(6)-C(5)-H(5)	121.7(13)	C(4)-C(5)-H(5)	122.8(13)
Fe(1)-C(5)-H(5)	122.6(13)	C(5)-C(6)-C(7)	114.4(2)
C(5)-C(6)-Fe(1)	70.06(14)	C(7)-C(6)-Fe(1)	70.85(13)
C(5)-C(6)-H(6)	120.6(13)	C(7)-C(6)-H(6)	124.6(13)
Fe(1)-C(6)-H(6)	122.0(13)	C(6)-C(7)-C(8)	120.5(2)
C(6)-C(7)-Fe(1)	68.98(14)	C(8)-C(7)-Fe(1)	109.90(15)
C(6)-C(7)-H(7)	122.6(15)	C(8)-C(7)-H(7)	108.4(15)
Fe(1)-C(7)-H(7)	121.1(16)	O(5)-C(8)-C(7)	111.56(18)
O(5)-C(8)-C(9)	111.12(18)	C(7)-C(8)-C(9)	110.23(18)
O(5)-C(8)-H(8)	107.9	C(7)-C(8)-H(8)	107.9
C(9)-C(8)-H(8)	107.9	O(4)-C(9)-C(4)	107.95(19)
O(4)-C(9)-C(10)	111.40(18)	C(4)-C(9)-C(10)	108.49(17)

O(4)-C(9)-C(8)	110.71(17)	C(4)-C(9)-C(8)	109.46(18)
C(10)-C(9)-C(8)	108.79(18)	O(6)-C(10)-O(7)	123.6(2)
O(6)-C(10)-C(9)	123.6(2)	O(7)-C(10)-C(9)	112.82(18)
O(7)-C(11)-H(11A)	109.5	O(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	O(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 27 Anisotropic displacement parameters ($Å^2$ x 10^3) for (±)-468. The anisotropic displacement actor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	15(1)	12(1)	10(1)	0(1)	4(1)	1(1)
O(1)	55(1)	56(2)	18(1)	13(1)	12(1)	-8(1)
O(2)	63(2)	18(1)	34(1)	-1(1)	17(1)	7(1)
O(3)	18(1)	52(1)	24(1)	-2(1)	-2(1)	10(1)
O(4)	9(1)	11(1)	16(1)	-2(1)	5(1)	-1(1)
O(5)	13(1)	9(1)	13(1)	-1(1)	4(1)	-2(1)
O(6)	10(1)	17(1)	18(1)	6(1)	0(1)	0(1)
O(7)	15(1)	16(1)	10(1)	3(1)	5(1)	3(1)
C(1)	25(2)	23(2)	14(2)	0(1)	1(1)	-2(1)
C(2)	26(2)	22(2)	14(1)	3(1)	8(1)	4(1)
C(3)	25(2)	16(1)	9(1)	-4(1)	0(1)	2(1)
C(4)	15(1)	8(1)	12(1)	3(1)	1(1)	2(1)
C(5)	12(1)	16(1)	12(1)	2(1)	1(1)	7(1)
C(6)	10(1)	19(1)	9(1)	-2(1)	4(1)	-2(1)
C(7)	17(1)	7(1)	10(1)	0(1)	2(1)	-2(1)
C(8)	9(1)	7(1)	9(1)	0(1)	0(1)	1(1)
C(9)	7(1)	9(1)	12(1)	2(1)	3(1)	2(1)
C(10)	12(1)	5(1)	14(1)	4(1)	4(1)	-1(1)
C(11)	24(2)	23(2)	12(1)	6(1)	3(1)	0(1)

Table 28 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (±)-468.

Atom	x	y	z	U(eq)
H(4A)	3780	7495	9506	34(9)
H(5A)	8602	11081	9607	28(8)
H(8)	5394	9361	8500	11
H(11A)	7469	6782	12615	29
H(11B)	6124	8331	12948	29
H(11C)	8251	8894	12656	29
H(4)	6830(30)	4503(14)	8700(20)	19(7)
H(5)	10110(20)	5280(20)	8414(18)	9(6)
H(6)	10816(16)	8160(30)	7790(17)	4(6)
H(7)	7970(40)	9950(20)	7580(20)	28(7)

Table 29 Dihedral angles [°] for (±)-468.

Atom1 - Atom2 - Atom3 - Atom4	Dihedral
C(3) - Fe(1) - C(1) - O(1)	110(9)
C(2) - Fe(1) - C(1) - O(1)	-148(9)
C(6) - Fe(1) - C(1) - O(1)	-25(9)
C(5) - Fe(1) - C(1) - O(1)	-53(9)
C(7) - Fe(1) - C(1) - O(1)	15(9)
C(4) - Fe(1) - C(1) - O(1)	-38(9)
C(3) - Fe(1) - C(2) - O(2)	-92(6)
C(1) - Fe(1) - C(2) - O(2)	167(6)

C(6) - Fe(1) - C(2) - O(2)	72(6)
C(5) - Fe(1) - C(2) - O(2)	45(6)
C(7) - Fe(1) - C(2) - O(2)	57(6)
C(4) - Fe(1) - C(2) - O(2)	5(6)
C(2) - Fe(1) - C(3) - O(3)	-156(8)
C(1) - Fe(1) - C(3) - O(3)	-60(8)
C(6) - Fe(1) - C(3) - O(3)	42(8)
C(5) - Fe(1) - C(3) - O(3)	99(8)
C(7) - Fe(1) - C(3) - O(3)	33(8)
C(4) - Fe(1) - C(3) - O(3)	110(8)
C(3) - Fe(1) - C(4) - C(5)	-167.27(15)
C(2) - Fe(1) - C(4) - C(5)	91.08(15)
C(1) - Fe(1) - C(4) - C(5)	-19.2(4)
C(6) - Fe(1) - C(4) - C(5)	-33.22(14)
C(7) - Fe(1) - C(4) - C(5)	-74.67(14)
C(3) - Fe(1) - C(4) - C(9)	-53.51(18)
C(2) - Fe(1) - C(4) - C(9)	-155.16(17)
C(1) - Fe(1) - C(4) - C(9)	94.5(4)
C(6) - Fe(1) - C(4) - C(9)	80.54(17)
C(5) - Fe(1) - C(4) - C(9)	113.8(2)
C(7) - Fe(1) - C(4) - C(9)	39.09(16)
C(9) - C(4) - C(5) - C(6)	-46.7(3)
Fe(1) - C(4) - C(5) - C(6)	56.48(18)
C(9) - C(4) - C(5) - Fe(1)	-103.18(19)
C(3) - Fe(1) - C(5) - C(6)	-108.84(18)
C(2) - Fe(1) - C(5) - C(6)	142.53(15)
C(1) - Fe(1) - C(5) - C(6)	46.31(18)
C(7) - Fe(1) - C(5) - C(6)	-33.61(14)
C(4) - Fe(1) - C(5) - C(6)	-126.7(2)
C(3) - Fe(1) - C(5) - C(4)	17.8(2)
C(2) - Fe(1) - C(5) - C(4)	-90.81(15)
C(1) - Fe(1) - C(5) - C(4)	172.96(15)
C(6) - Fe(1) - C(5) - C(4)	126.7(2)
C(7) - Fe(1) - C(5) - C(4)	93.04(14)
C(4) - C(5) - C(6) - C(7)	-0.7(3)
Fe(1) - C(5) - C(6) - C(7)	56.78(18)
C(4) - C(5) - C(6) - Fe(1)	-57.44(18)
C(3) - Fe(1) - C(6) - C(5)	111.67(17)
C(2) - Fe(1) - C(6) - C(5)	-46.41(18)
C(1) - Fe(1) - C(6) - C(5)	-142.41(15)
C(7) - Fe(1) - C(6) - C(5)	126.2(2)
C(4) - Fe(1) - C(6) - C(5)	33.23(13)
C(3) - Fe(1) - C(6) - C(7)	-14.6(2)
C(2) - Fe(1) - C(6) - C(7)	-172.66(15)
C(1) - Fe(1) - C(6) - C(7)	91.34(15)
C(5) - Fe(1) - C(6) - C(7)	-126.2(2)
C(4) - Fe(1) - C(6) - C(7)	-93.02(14)
C(5) - C(6) - C(7) - C(8)	45.0(3)
Fe(1) - C(6) - C(7) - C(8)	101.4(2)
C(5) - C(6) - C(7) - Fe(1)	-56.36(19)
C(3) - Fe(1) - C(7) - C(6)	169.39(15)
C(2) - Fe(1) - C(7) - C(6)	20.6(4)
C(1) - Fe(1) - C(7) - C(6)	-90.42(15)
C(5) - Fe(1) - C(7) - C(6)	33.41(14)
C(4) - Fe(1) - C(7) - C(6)	74.59(14)
C(3) - Fe(1) - C(7) - C(8)	53.39(17)
C(2) - Fe(1) - C(7) - C(8)	-95.4(4)
C(1) - Fe(1) - C(7) - C(8)	153.58(17)
C(6) - Fe(1) - C(7) - C(8)	-116.0(2)
C(5) - Fe(1) - C(7) - C(8)	-82.60(16)
C(4) - Fe(1) - C(7) - C(8)	-41.42(15)
C(6) - C(7) - C(8) - O(5)	83.9(3)
Fe(1) - C(7) - C(8) - O(5)	160.63(14)
C(6) - C(7) - C(8) - C(9)	-40.0(3)
Fe(1) - C(7) - C(8) - C(9)	36.7(2)
C(5) - C(4) - C(9) - O(4)	168.19(19)
Fe(1) - C(4) - C(9) - O(4)	91.99(18)
C(5) - C(4) - C(9) - C(10)	-71.0(3)
Fe(1) - C(4) - C(9) - C(10)	-147.16(15)
C(5) - C(4) - C(9) - C(8)	47.6(3)

Fe(1) - C(4) - C(9) - C(8)	-28.6(2)
O(5) - C(8) - C(9) - O(4)	111.96(19)
C(7) - C(8) - C(9) - O(4)	-123.84(19)
O(5) - C(8) - C(9) - C(4)	-129.15(19)
C(7) - C(8) - C(9) - C(4)	-5.0(2)
O(5) - C(8) - C(9) - C(10)	-10.8(2)
C(7) - C(8) - C(9) - C(10)	113.4(2)
C(11) - O(7) - C(10) - O(6)	-3.7(3)
C(11) - O(7) - C(10) - C(9)	176.57(18)
O(4) - C(9) - C(10) - O(6)	157.5(2)
C(4) - C(9) - C(10) - O(6)	38.8(3)
C(8) - C(9) - C(10) - O(6)	-80.2(3)
O(4) - C(9) - C(10) - O(7)	-22.8(3)

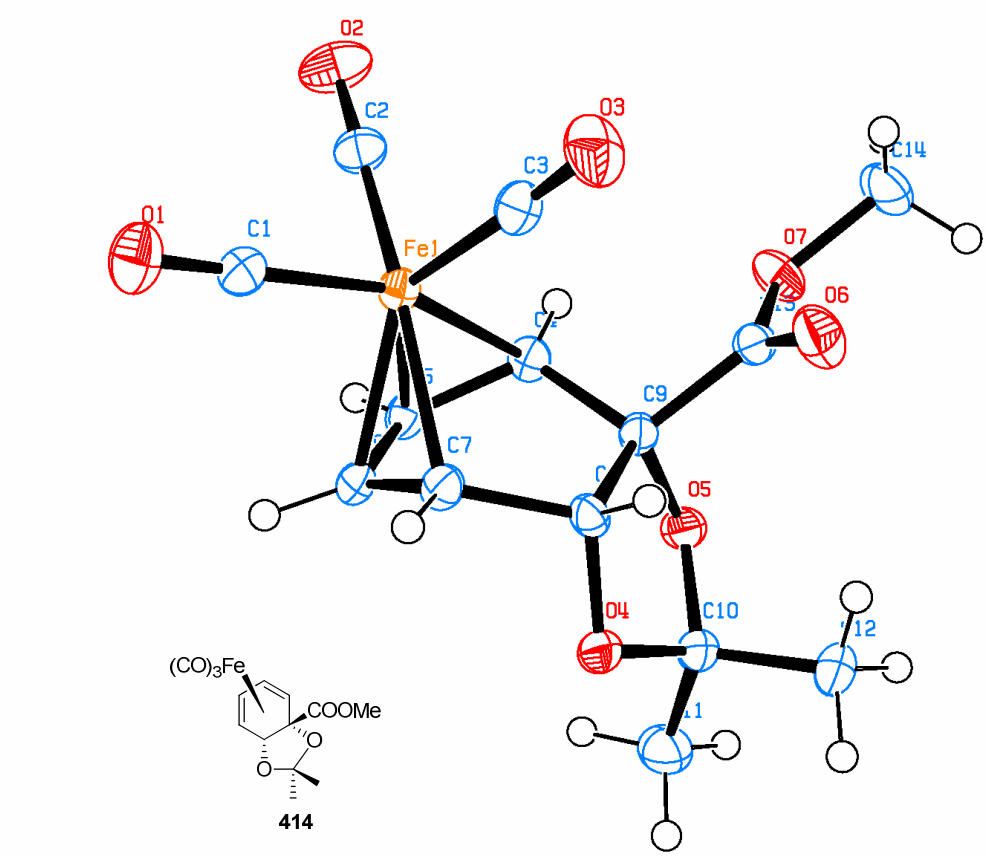


Figure 16 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **414**

Table 30 Crystal data and structure refinement for 414

Identification code	k10sel1
Empirical formula	C14 H14 Fe O7
Formula weight	350.10
Temperature	150(2) K

Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 20.7320(4)Å $\alpha = 90^o$
	b = 6.2630(1)Å $\beta = 110.174(1)^o$
	c = 12.1540(3)Å $\gamma = 90^o$
Volume	1481.31(5) $Å^3$
Z	4
Density (calculated)	1.570 Mg/m^3
Absorption coefficient	1.050 mm^{-1}
F(000)	720
Crystal size	0.30 x 0.20 x 0.15 mm
Theta range for data collection	3.57 to 27.48^o
Index ranges	-26<=h<=26; -8<=k<=8; -15<=l<=15
Reflections collected	12804
Independent reflections	3350 [R(int) = 0.1159]
Reflections observed (>2σ)	3232
Data Completeness	0.995
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.750 and 0.155
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3350 / 5 / 219
Goodness-of-fit on F^2	1.023
Final R indices [I>2σ(I)]	R1 = 0.0398 wR2 = 0.0975
R indices (all data)	R1 = 0.0438 wR2 = 0.0992
Absolute structure parameter	-0.009(16)
Largest diff. peak and hole	0.667 and -0.694 $eÅ^{-3}$

Notes:

H4-H7 located and refine at 0.98Å from the relevant parent atoms.

Table 31 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 414. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	3048(1)	470(1)	2711(1)	19(1)
O(1)	4438(1)	-1348(4)	3628(2)	39(1)
O(2)	3601(1)	4600(4)	2320(2)	40(1)
O(3)	2626(1)	-1181(4)	301(2)	39(1)
O(4)	1466(1)	-2575(3)	3448(2)	24(1)
O(5)	1019(1)	640(4)	2734(2)	24(1)
O(6)	1103(1)	-976(3)	224(2)	35(1)
O(7)	1050(1)	2505(3)	618(2)	30(1)
C(1)	3895(2)	-662(4)	3266(2)	25(1)
C(2)	3385(2)	2991(4)	2462(3)	26(1)
C(3)	2775(2)	-528(4)	1233(2)	25(1)
C(4)	2124(2)	1879(4)	2707(2)	20(1)
C(5)	2607(2)	1656(4)	3872(3)	21(1)
C(6)	2854(2)	-438(5)	4196(2)	21(1)
C(7)	2579(1)	-2022(4)	3316(2)	20(1)
C(8)	1815(1)	-1994(4)	2651(2)	19(1)
C(9)	1551(1)	275(5)	2241(2)	19(1)
C(10)	845(1)	-1372(4)	3124(2)	25(1)

C(11)	659(2)	-962(5)	4200(3)	36(1)
C(12)	280(2)	-2513(5)	2158(3)	35(1)
C(13)	1218(1)	452(6)	909(2)	22(1)
C(14)	709(2)	2955(5)	-611(3)	35(1)

Table 32 Bond lengths [Å] and angles [^{o}] for 414.

Fe(1)-C(2)	1.795(3)	Fe(1)-C(1)	1.795(3)
Fe(1)-C(3)	1.799(3)	Fe(1)-C(6)	2.060(3)
Fe(1)-C(5)	2.066(3)	Fe(1)-C(7)	2.101(2)
Fe(1)-C(4)	2.107(3)	O(1)-C(1)	1.143(4)
O(2)-C(2)	1.139(4)	O(3)-C(3)	1.142(4)
O(4)-C(10)	1.426(3)	O(4)-C(8)	1.442(3)
O(5)-C(10)	1.436(3)	O(5)-C(9)	1.443(3)
O(6)-C(13)	1.189(4)	O(7)-C(13)	1.347(4)
O(7)-C(14)	1.443(4)	C(4)-C(5)	1.431(4)
C(4)-C(9)	1.509(4)	C(4)-H(4)	0.980(5)
C(5)-C(6)	1.414(4)	C(5)-H(5)	0.979(5)
C(6)-C(7)	1.426(4)	C(6)-H(6)	0.979(5)
C(7)-C(8)	1.509(4)	C(7)-H(7)	0.982(5)
C(8)-C(9)	1.543(4)	C(8)-H(8)	1.0000
C(9)-C(13)	1.530(3)	C(10)-C(11)	1.508(4)
C(10)-C(12)	1.521(4)	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(2)-Fe(1)-C(1)	91.32(13)	C(2)-Fe(1)-C(3)	98.29(13)
C(1)-Fe(1)-C(3)	99.69(13)	C(2)-Fe(1)-C(6)	126.54(12)
C(1)-Fe(1)-C(6)	91.28(12)	C(3)-Fe(1)-C(6)	133.65(12)
C(2)-Fe(1)-C(5)	95.09(12)	C(1)-Fe(1)-C(5)	119.39(12)
C(3)-Fe(1)-C(5)	138.26(12)	C(6)-Fe(1)-C(5)	40.07(10)
C(2)-Fe(1)-C(7)	165.20(11)	C(1)-Fe(1)-C(7)	94.92(11)
C(3)-Fe(1)-C(7)	93.89(11)	C(6)-Fe(1)-C(7)	40.06(10)
C(5)-Fe(1)-C(7)	70.16(10)	C(2)-Fe(1)-C(4)	92.18(12)
C(1)-Fe(1)-C(4)	159.44(12)	C(3)-Fe(1)-C(4)	99.84(12)
C(6)-Fe(1)-C(4)	70.48(11)	C(5)-Fe(1)-C(4)	40.09(11)
C(7)-Fe(1)-C(4)	77.40(10)	C(10)-O(4)-C(8)	107.26(19)
C(10)-O(5)-C(9)	108.3(2)	C(13)-O(7)-C(14)	116.6(2)
O(1)-C(1)-Fe(1)	178.8(3)	O(2)-C(2)-Fe(1)	179.0(3)
O(3)-C(3)-Fe(1)	177.5(3)	C(5)-C(4)-C(9)	119.8(2)
C(5)-C(4)-Fe(1)	68.41(15)	C(9)-C(4)-Fe(1)	108.59(16)
C(5)-C(4)-H(4)	118(2)	C(9)-C(4)-H(4)	114(2)
Fe(1)-C(4)-H(4)	121(2)	C(6)-C(5)-C(4)	115.4(2)
C(6)-C(5)-Fe(1)	69.72(17)	C(4)-C(5)-Fe(1)	71.50(15)
C(6)-C(5)-H(5)	123(2)	C(4)-C(5)-H(5)	121(2)
Fe(1)-C(5)-H(5)	121(2)	C(5)-C(6)-C(7)	115.0(2)
C(5)-C(6)-Fe(1)	70.21(17)	C(7)-C(6)-Fe(1)	71.54(15)
C(5)-C(6)-H(6)	122.4(18)	C(7)-C(6)-H(6)	121.9(18)
Fe(1)-C(6)-H(6)	120.0(19)	C(6)-C(7)-C(8)	118.0(2)
C(6)-C(7)-Fe(1)	68.40(14)	C(8)-C(7)-Fe(1)	109.29(16)
C(6)-C(7)-H(7)	119(2)	C(8)-C(7)-H(7)	113(2)
Fe(1)-C(7)-H(7)	122(2)	O(4)-C(8)-C(7)	108.3(2)
O(4)-C(8)-C(9)	104.16(19)	C(7)-C(8)-C(9)	111.9(2)
O(4)-C(8)-H(8)	110.8	C(7)-C(8)-H(8)	110.8
C(9)-C(8)-H(8)	110.8	O(5)-C(9)-C(4)	110.7(2)
O(5)-C(9)-C(13)	107.25(19)	C(4)-C(9)-C(13)	111.0(2)
O(5)-C(9)-C(8)	104.4(2)	C(4)-C(9)-C(8)	110.3(2)
C(13)-C(9)-C(8)	112.9(2)	O(4)-C(10)-O(5)	104.3(2)
O(4)-C(10)-C(11)	109.1(2)	O(5)-C(10)-C(11)	107.8(2)
O(4)-C(10)-C(12)	110.3(2)	O(5)-C(10)-C(12)	111.9(2)
C(11)-C(10)-C(12)	113.0(3)	C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5

H(12B)-C(12)-H(12C)	109.5	O(6)-C(13)-O(7)	124.3(2)
O(6)-C(13)-C(9)	126.5(3)	O(7)-C(13)-C(9)	109.2(3)
O(7)-C(14)-H(14A)	109.5	O(7)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	O(7)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 33 Anisotropic displacement parameters ($Å^2$ x 10^3) for 414. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	18(1)	16(1)	20(1)	-1(1)	6(1)	0(1)
O(1)	25(1)	42(1)	45(1)	0(1)	8(1)	6(1)
O(2)	50(2)	23(1)	56(2)	-3(1)	32(1)	-9(1)
O(3)	42(1)	47(1)	26(1)	-13(1)	9(1)	2(1)
O(4)	19(1)	25(1)	28(1)	8(1)	6(1)	-1(1)
O(5)	20(1)	24(1)	27(1)	7(1)	9(1)	3(1)
O(6)	42(1)	32(1)	25(1)	-1(1)	1(1)	-2(1)
O(7)	35(1)	27(1)	24(1)	10(1)	6(1)	10(1)
C(1)	23(2)	25(1)	26(1)	1(1)	8(1)	-3(1)
C(2)	27(2)	26(1)	28(1)	-1(1)	14(1)	1(1)
C(3)	20(1)	26(1)	28(2)	-1(1)	7(1)	1(1)
C(4)	20(1)	15(1)	24(1)	1(1)	7(1)	3(1)
C(5)	17(1)	23(1)	22(1)	-6(1)	7(1)	-1(1)
C(6)	15(1)	26(1)	22(1)	1(1)	6(1)	-1(1)
C(7)	18(1)	18(1)	25(1)	1(1)	7(1)	1(1)
C(8)	20(1)	16(1)	18(1)	2(1)	3(1)	0(1)
C(9)	17(1)	18(1)	20(1)	1(1)	4(1)	-1(1)
C(10)	18(1)	28(1)	26(1)	8(1)	5(1)	-1(1)
C(11)	30(2)	47(2)	33(2)	10(1)	15(1)	4(1)
C(12)	21(2)	43(2)	34(2)	9(1)	0(1)	-9(1)
C(13)	17(1)	24(1)	24(1)	8(1)	6(1)	2(1)
C(14)	33(2)	43(2)	26(1)	16(1)	5(1)	10(1)

Table 34 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 414

Atom	x	y	z	U(eq)
H(8)	1694	-3001	1971	23
H(11A)	1037	-209	4787	54
H(11B)	576	-2325	4525	54
H(11C)	242	-86	3988	54
H(12A)	-143	-1664	1939	53
H(12B)	197	-3917	2440	53
H(12C)	421	-2693	1473	53
H(14A)	966	2298	-1064	53
H(14B)	688	4503	-735	53
H(14C)	242	2370	-867	53
H(6)	3236(11)	-740(50)	4921(15)	21(8)
H(7)	2772(17)	-3470(20)	3450(30)	26(8)
H(5)	2801(18)	2910(40)	4350(30)	31(9)
H(4)	1998(19)	3320(30)	2400(30)	43(13)

Table 35 Dihedral angles [^{o}] for 414.

Atom1 - Atom2 - Atom3 - Atom4	Dihedral

C(2) - Fe(1) - C(1) - O(1)	35(13)
C(3) - Fe(1) - C(1) - O(1)	134(13)
C(6) - Fe(1) - C(1) - O(1)	-91(13)
C(5) - Fe(1) - C(1) - O(1)	-61(13)
C(7) - Fe(1) - C(1) - O(1)	-131(13)
C(4) - Fe(1) - C(1) - O(1)	-65(13)
C(1) - Fe(1) - C(2) - O(2)	-88(18)
C(3) - Fe(1) - C(2) - O(2)	172(100)
C(6) - Fe(1) - C(2) - O(2)	5(18)
C(5) - Fe(1) - C(2) - O(2)	32(18)
C(7) - Fe(1) - C(2) - O(2)	27(18)
C(4) - Fe(1) - C(2) - O(2)	72(18)
C(2) - Fe(1) - C(3) - O(3)	79(6)
C(1) - Fe(1) - C(3) - O(3)	-14(6)
C(6) - Fe(1) - C(3) - O(3)	-115(6)
C(5) - Fe(1) - C(3) - O(3)	-174(6)
C(7) - Fe(1) - C(3) - O(3)	-109(6)
C(4) - Fe(1) - C(3) - O(3)	173(6)
C(2) - Fe(1) - C(4) - C(5)	-95.31(17)
C(1) - Fe(1) - C(4) - C(5)	4.3(4)
C(3) - Fe(1) - C(4) - C(5)	165.89(16)
C(6) - Fe(1) - C(4) - C(5)	32.91(15)
C(7) - Fe(1) - C(4) - C(5)	74.07(16)
C(2) - Fe(1) - C(4) - C(9)	149.13(19)
C(1) - Fe(1) - C(4) - C(9)	-111.3(3)
C(3) - Fe(1) - C(4) - C(9)	50.3(2)
C(6) - Fe(1) - C(4) - C(9)	-82.65(18)
C(5) - Fe(1) - C(4) - C(9)	-115.6(2)
C(7) - Fe(1) - C(4) - C(9)	-41.49(17)
C(9) - C(4) - C(5) - C(6)	44.0(4)
Fe(1) - C(4) - C(5) - C(6)	-55.7(2)
C(9) - C(4) - C(5) - Fe(1)	99.7(2)
C(2) - Fe(1) - C(5) - C(6)	-145.36(17)
C(1) - Fe(1) - C(5) - C(6)	-50.97(19)
C(3) - Fe(1) - C(5) - C(6)	106.2(2)
C(7) - Fe(1) - C(5) - C(6)	33.38(16)
C(4) - Fe(1) - C(5) - C(6)	127.3(2)
C(2) - Fe(1) - C(5) - C(4)	87.34(17)
C(1) - Fe(1) - C(5) - C(4)	-178.27(16)
C(3) - Fe(1) - C(5) - C(4)	-21.1(2)
C(6) - Fe(1) - C(5) - C(4)	-127.3(2)
C(7) - Fe(1) - C(5) - C(4)	-93.92(16)
C(4) - C(5) - C(6) - C(7)	-0.7(4)
Fe(1) - C(5) - C(6) - C(7)	-57.3(2)
C(4) - C(5) - C(6) - Fe(1)	56.6(2)
C(2) - Fe(1) - C(6) - C(5)	44.8(2)
C(1) - Fe(1) - C(6) - C(5)	137.39(17)
C(3) - Fe(1) - C(6) - C(5)	-117.89(19)
C(7) - Fe(1) - C(6) - C(5)	-126.5(2)
C(4) - Fe(1) - C(6) - C(5)	-32.92(15)
C(2) - Fe(1) - C(6) - C(7)	171.28(17)
C(1) - Fe(1) - C(6) - C(7)	-96.13(17)
C(3) - Fe(1) - C(6) - C(7)	8.6(2)
C(5) - Fe(1) - C(6) - C(7)	126.5(2)
C(4) - Fe(1) - C(6) - C(7)	93.55(17)
C(5) - C(6) - C(7) - C(8)	-44.4(3)
Fe(1) - C(6) - C(7) - C(8)	-101.1(2)
C(5) - C(6) - C(7) - Fe(1)	56.6(2)
C(2) - Fe(1) - C(7) - C(6)	-28.5(6)
C(1) - Fe(1) - C(7) - C(6)	86.13(18)
C(3) - Fe(1) - C(7) - C(6)	-173.79(18)
C(5) - Fe(1) - C(7) - C(6)	-33.38(16)
C(4) - Fe(1) - C(7) - C(6)	-74.56(17)
C(2) - Fe(1) - C(7) - C(8)	84.9(5)
C(1) - Fe(1) - C(7) - C(8)	-160.55(18)
C(3) - Fe(1) - C(7) - C(8)	-60.46(18)
C(6) - Fe(1) - C(7) - C(8)	113.3(2)
C(5) - Fe(1) - C(7) - C(8)	79.94(18)
C(4) - Fe(1) - C(7) - C(8)	38.76(17)
C(10) - O(4) - C(8) - C(7)	144.9(2)

C(10) - O(4) - C(8) - C(9)	25.7(3)
C(6) - C(7) - C(8) - O(4)	-68.2(3)
Fe(1) - C(7) - C(8) - O(4)	-143.37(16)
C(6) - C(7) - C(8) - C(9)	46.1(3)
Fe(1) - C(7) - C(8) - C(9)	-29.1(2)
C(10) - O(5) - C(9) - C(4)	-133.0(2)
C(10) - O(5) - C(9) - C(13)	105.8(3)
C(10) - O(5) - C(9) - C(8)	-14.3(3)
C(5) - C(4) - C(9) - O(5)	75.9(3)
Fe(1) - C(4) - C(9) - O(5)	151.17(16)
C(5) - C(4) - C(9) - C(13)	-165.1(2)
Fe(1) - C(4) - C(9) - C(13)	-89.8(2)
C(5) - C(4) - C(9) - C(8)	-39.2(3)
Fe(1) - C(4) - C(9) - C(8)	36.1(2)
O(4) - C(8) - C(9) - O(5)	-6.8(2)
C(7) - C(8) - C(9) - O(5)	-123.6(2)
O(4) - C(8) - C(9) - C(4)	112.2(2)
C(7) - C(8) - C(9) - C(4)	-4.6(3)
O(4) - C(8) - C(9) - C(13)	-122.9(2)
C(7) - C(8) - C(9) - C(13)	120.3(2)
C(8) - O(4) - C(10) - O(5)	-34.9(3)
C(8) - O(4) - C(10) - C(11)	-149.9(2)
C(8) - O(4) - C(10) - C(12)	85.4(2)
C(9) - O(5) - C(10) - O(4)	30.3(3)
C(9) - O(5) - C(10) - C(11)	146.3(2)
C(9) - O(5) - C(10) - C(12)	-88.9(3)
C(14) - O(7) - C(13) - O(6)	0.1(4)
C(14) - O(7) - C(13) - C(9)	-178.2(2)
O(5) - C(9) - C(13) - O(6)	-108.0(3)
C(4) - C(9) - C(13) - O(6)	130.9(3)
C(8) - C(9) - C(13) - O(6)	6.4(4)
O(5) - C(9) - C(13) - O(7)	70.3(3)
C(4) - C(9) - C(13) - O(7)	-50.8(3)
C(8) - C(9) - C(13) - O(7)	-175.3(2)

Symmetry transformations used to generate equivalent atoms:

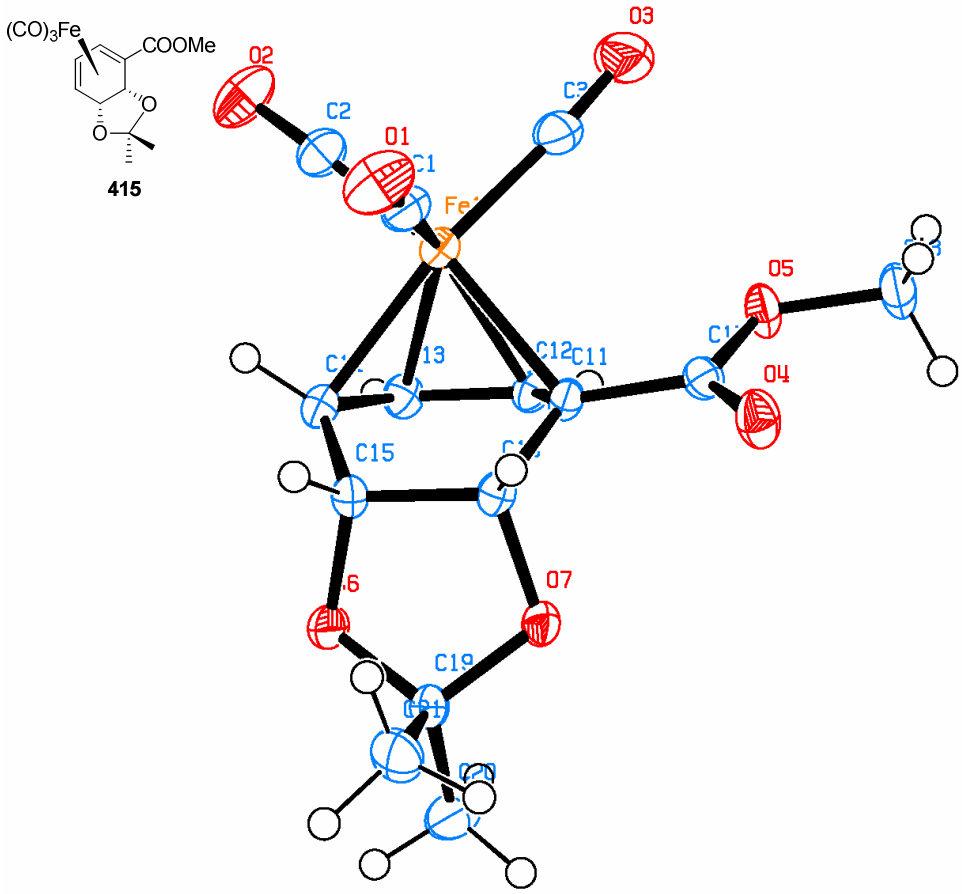


Figure 17 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **415.**

Table 36 Crystal data and structure refinement for 415

Identification code	h09sel5
Empirical formula	C14 H14 Fe O7
Formula weight	350.10
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 10.1710(4) Å b = 7.2170(4) Å c = 10.6320(6) Å
Volume	731.36(6) $Å^3$
Z	2
Density (calculated)	1.590 Mg/m^3
Absorption coefficient	1.063 mm^{-1}

F(000)	360
Crystal size	0.22 x 0.17 x 0.13 mm^3
Theta range for data collection	8.57 to 30.69°.
Index ranges	-14<=h<=14, -10<=k<=10, -15<=l<=15
Reflections collected	7011
Independent reflections	3709 [R(int) = 0.0767]
Completeness to theta = 30.69°	92.9 %
Absorption correction	None
Max. and min. transmission	0.8742 and 0.7998
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3709 / 1 / 203
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.1013
R indices (all data)	R1 = 0.0402, wR2 = 0.1034
Absolute structure parameter	-0.005(16)
Extinction coefficient	0.030(11)
Largest diff. peak and hole	0.427 and -0.616 e.$Å^{-3}$

Table 37 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **415**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

ATOM	X	Y	Z	U(eq)
Fe(1)	-1414(1)	1264(1)	-8094(1)	19(1)
O(1)	812(2)	-1126(3)	-6360(2)	38(1)
O(2)	-49(3)	4784(3)	6992(3)	42(1)
O(3)	-584(2)	1747(4)	10470(2)	45(1)
O(4)	-2697(2)	-3871(3)	-9759(2)	28(1)
O(5)	-2932(2)	-1314(3)	-11032(2)	26(1)
O(6)	-4070(2)	-727(3)	-6166(2)	26(1)
O(7)	-4310(2)	-2720(2)	-7867(2)	21(1)
C(1)	-47(3)	-209(4)	-7048(3)	24(1)
C(2)	-589(3)	3439(4)	-7459(3)	27(1)
C(3)	-933(2)	1517(5)	-9585(3)	29(1)
C(11)	-2875(2)	-917(3)	-8810(2)	18(1)
C(12)	-3521(2)	868(3)	-9167(2)	19(1)
C(13)	-3357(2)	2090(3)	-8080(2)	22(1)
C(14)	-2559(2)	1389(4)	-6780(2)	21(1)
C(15)	-2771(2)	-571(3)	-6412(2)	19(1)
C(16)	-2951(2)	-1911(3)	-7589(2)	19(1)
C(17)	-2816(2)	-2208(3)	-9881(2)	19(1)
C(18)	-2958(3)	-2485(4)	-12142(3)	28(1)
C(19)	-4665(2)	-2481(3)	-6692(2)	21(1)
C(20)	-6244(3)	-2359(4)	-7107(3)	33(1)
C(21)	-4039(3)	-4034(4)	-5700(2)	30(1)

Table 38 Bond lengths [Å] and angles [°] for 415

Fe(1)- C(1)	1.794(3)	C(12)-C(11)-C(16)	119.87(19)
Fe(1)- C(2	1.796(3)	C(17)-C(11)-C(16)	112.85(19)
Fe(1) -C(3)	1.824(3)	C(12)-C(11)-Fe(1)	68.08(12)
Fe(1) -C(12)	2.066(2)	C(17)-C(11)-Fe(1)	122.02(16)
Fe(1)- C(13)	2.070(2)	C(16)-C(11)-Fe(1)	106.54(14)
Fe(1)- C(14)	2.109(2)	C(13)-C(12)-C(11)	115.50(19)
Fe(1)- C(11)	2.116(2)	C(13)-C(12)-Fe(1)	70.11(12)
O(1) -C(1)	1.136(3)	C(11)-C(12)-Fe(1)	71.79(12)
O(2) -C(2)	1.140(4)	C(13)-C(12)-H(12)	122.2
O(3)- C(3)	1.129(3)	C(11)-C(12)-H(12)	122.2

O(4) -C(17)	1.209(3)	Fe(1)-C(12)-H(12)	127.7
O(5)-C(17)	1.351(3)	C(12)-C(13)-C(14)	115.7(2)
O(5) -C(18)	1.445(3)	C(12)-C(13)-Fe(1)	69.84(13)
O(6)- C(19)	1.430(3)	C(14)-C(13)-Fe(1)	71.50(13)
O(6) -C(15)	1.438(3)	C(12)-C(13)-H(13)	122.2
O(7)- C(19)	1.426(3)	C(14)-C(13)-H(13)	122.2
O(7)- C(16)	1.434(3)	Fe(1)-C(13)-H(13)	128.5
C(11)- C(12)	1.436(3)	C(13)-C(14)-C(15)	120.0(2)
C(11)- C(17)	1.489(3)	C(13)-C(14)-Fe(1)	68.52(13)
C(11)- C(16)	1.509(3)	C(15)-C(14)-Fe(1)	107.15(16)
C(1)-Fe(1)-C(2)	97.23(12)	C(13)-C(14)-H(14)	120.0
C(1)-Fe(1)-C(3)	102.31(12)	C(15)-C(14)-H(14)	120.0
C(2)-Fe(1)-C(3)	90.42(13)	Fe(1)-C(14)-H(14)	94.1
C(1)-Fe(1)-C(12)	133.62(10)	O(6)-C(15)-C(14)	110.21(19)
C(2)-Fe(1)-C(12)	125.92(11)	O(6)-C(15)-C(16)	104.00(17)
C(3)-Fe(1)-C(12)	94.30(10)	C(14)-C(15)-C(16)	111.49(18)
C(1)-Fe(1)-C(13)	134.54(10)	O(6)-C(15)-H(15)	110.3
C(2)-Fe(1)-C(13)	93.90(11)	C(14)-C(15)-H(15)	110.3
C(3)-Fe(1)-C(13)	121.59(11)	C(16)-C(15)-H(15)	110.3
C(12)-Fe(1)-C(13	40.05(9)	O(7)-C(16)-C(11)	110.60(17)
C(1)-Fe(1)-C(14)	95.86(11)	O(7)-C(16)-C(15)	104.84(17)
C(2)-Fe(1)-C(14)	90.44(12)	C(11)-C(16)-C(15)	111.89(19)
C(3)-Fe(1)-C(14)	161.55(11)	O(7)-C(16)-H(16)	109.8
C(12)-Fe(1)-C(14)	70.46(8)	C(11)-C(16)-H(16)	109.8
C(13)-Fe(1)-C(14)	39.98(9)	C(15)-C(16)-H(16)	109.8
C(1)-Fe(1)-C(11)	94.41(10)	O(4)-C(17)-O(5)	123.1(2)
C(2)-Fe(1)-C(11)	164.26(11)	O(4)-C(17)-C(11)	124.6(2)
C(3)-Fe(1)-C(11)	97.43(11)	O(5)-C(17)-C(11)	112.29(19)
C(12)-Fe(1)-C(11)	40.14(8)	O(5)-C(18)-H(18A)	109.5
C(13)-Fe(1)-C(11)	70.37(9)	O(5)-C(18)-H(18B)	109.5
C(14)-Fe(1)-C(11)	77.83(9)	H(18A)-C(18)-H(18B)	109.5
C(17)-O(5)-C(18)	115.5(2)	O(5)-C(18)-H(18C)	109.5
C(19)-O(6)-C(15)	106.77(17)	H(18A)-C(18)-H(18C)	109.5
C(19)-O(7)-C(16)	106.91(16)	H(18B)-C(18)-H(18C)	109.5
O(1)-C(1)-Fe(1)	178.4(3)	O(7)-C(19)-O(6)	104.33(18)
O(2)-C(2)-Fe(1)	176.5(3)	O(7)-C(19)-C(20)	108.6(2)
O(3)-C(3)-Fe(1)	176.2(3)	O(6)-C(19)-C(20)	108.90(19)
C(12)-C(11)-C(17)	119.77(19)	O(7)-C(19)-C(21)	110.3(2)
H(20B)-C(20)-H(20C)	109.5	O(6)-C(19)-C(21)	111.3(2)
C(19)-C(21)-H(21A)	109.5	C(20)-C(19)-C(21)	113.0(2)
C(19)-C(21)-H(21B)	109.5	C(19)-C(20)-H(20A)	109.5
H(21A)-C(21)-H(21B)	109.5	C(19)-C(20)-H(20B)	109.5
C(19)-C(21)-H(21C)	109.5	H(20A)-C(20)-H(20B)	109.5
H(21A)-C(21)-H(21C)	109.5	C(19)-C(20)-H(20C)	109.5
H(21B)-C(21)-H(21C)	109.5	H(20A)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 39Anisotropic displacement parameters ($Å^2$x 10^3)for 415. The anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11 + ... + 2 h k a* b* U12]

ATOM	U1	U22	U33	U23	U13	U12
Fe(1)	18(1)	17(1)	19(1)	0(1)	4(1)	-1(1)
O(1)	27(1)	33(1)	44(1)	9(1)	-1(1)	4(1)
O(2)	40(1)	24(1)	52(1)	-5(1)	4(1)	-8(1)
O(3)	38(1)	67(2)	33(1)	1(1)	15(1)	-13(1)
O(4)	43(1)	18(1)	25(1)	-1(1)	15(1)	2(1)
O(5)	40(1)	19(1)	18(1)	-3(1)	12(1)	0(1)
O(6)	28(1)	24(1)	30(1)	-12(1)	16(1)	-7(1)
O(7)	24(1)	22(1)	16(1)	-3(1)	6(1)	-6(1)
C(1)	20(1)	23(1)	29(1)	-2(1)	7(1)	-4(1)
C(2)	26(1)	23(1)	30(1)	1(1)	7(1)	-1(1)
C(3)	21(1)	35(2)	28(1)	0(1)	7(1)	-5(1)
C(11)	19(1)	16(1)	16(1)	-2(1)	4(1)	-2(1)
C(12)	19(1)	19(1)	19(1)	0(1)	5(1)	0(1)
C(13)	22(1)	17(1)	25(1)	-2(1)	6(1)	1(1)
C(14)	22(1)	21(1)	20(1)	-3(1)	6(1)	-3(1)

C(15)	19(1)	22(1)	16(1)	-3(1)	5(1)	-1(1)
C(16)	19(1)	18(1)	18(1)	-1(1)	4(1)	0(1)
C(17)	19(1)	20(1)	18(1)	-1(1)	6(1)	1(1)
C(18)	43(1)	24(1)	22(1)	-6(1)	15(1)	0(1)
C(19)	24(1)	20(1)	22(1)	-5(1)	10(1)	-2(1)
C(20)	25(1)	24(1)	51(2)	-11(1)	17(1)	-2(1)
C(21)	39(1)	28(2)	23(1)	6(1)	11(1)	-1(1)

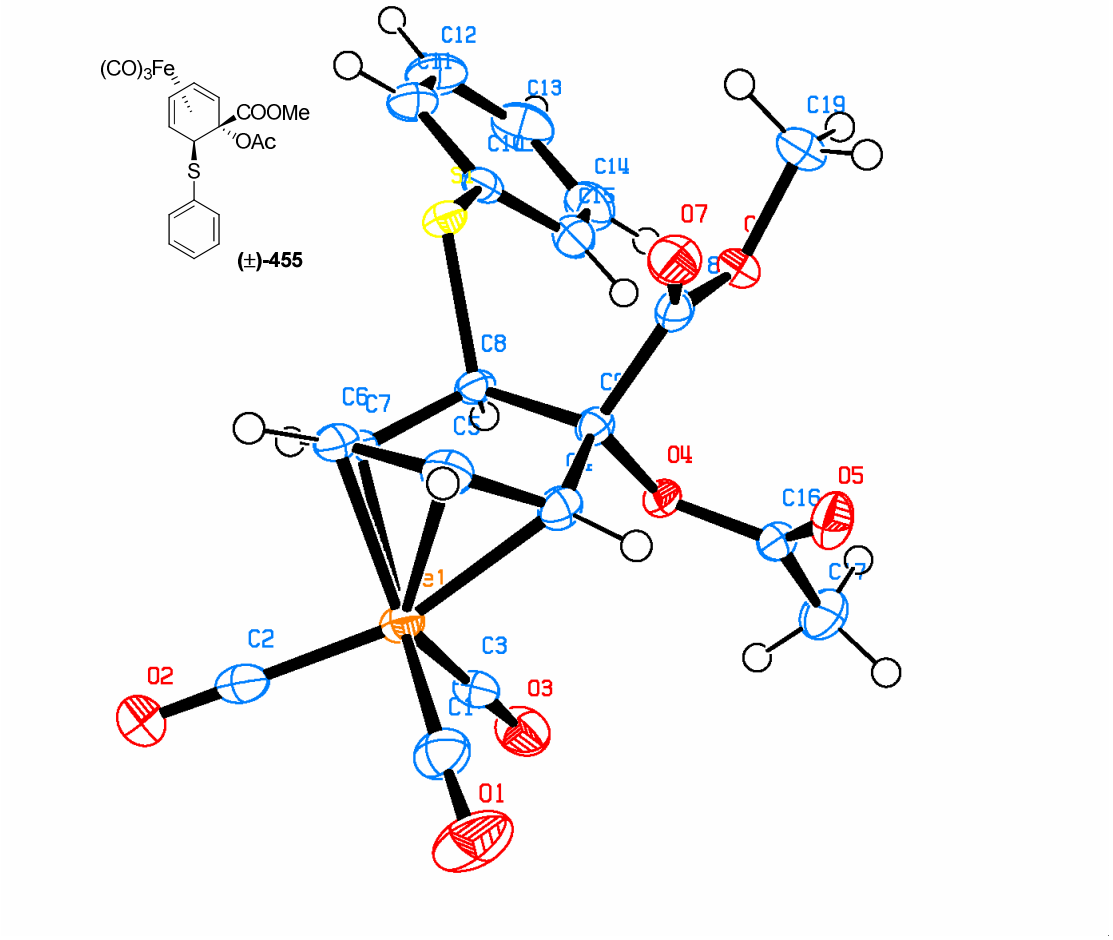


Figure 27 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **455**

Table 40 Crystal data and structure refinement 455

Identification code	k09sel4
Empirical formula	C19 H16 Fe O7 S
Formula weight	444.23
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	P-1
Unit cell dimensions	a = 7.3200(1)Å α = 97.505(1)°
	b = 10.5210(2)Å β = 103.386(1)°
	c = 13.3490(2)Å γ = 102.216(1)°
Volume	959.88(3) $Å^3$
Z	2
Density (calculated)	1.537 Mg/m^3
Absorption coefficient	0.933 mm^{-1}
F(000)	456
Crystal size	0.5 x 0.25 x 0.15 mm
Theta range for data collection	3.70 to 27.50°
Index ranges	-9<=h<=9; -13<=k<=13; -17<=l<=17
Reflections collected	18914
Independent reflections	4407 [R(int) = 0.0373]
Reflections observed (>2σ)	3921
Data Completeness	0.996
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.760 and 0.721
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4407 / 4 / 272
Goodness-of-fit on F^2	1.062
Final R indices [I>2σ(I)]	R1 = 0.0285 wR2 = 0.0690
R indices (all data)	R1 = 0.0358 wR2 = 0.0723
Largest diff. peak and hole	0.362 and -0.544 $eÅ^{-3}$

Notes:

H4-7 located and refined at 0.98Å from the relevant parent atoms. Structure is a racemic mixture.

Table 41 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 455. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	3416(1)	-2586(1)	1502(1)	20(1)
S(1)	3860(1)	1828(1)	1522(1)	21(1)
O(1)	942(2)	-5270(1)	1201(1)	49(1)
O(2)	6391(2)	-3497(1)	659(1)	34(1)
O(3)	5220(2)	-2322(1)	3752(1)	34(1)
O(4)	2642(2)	-388(1)	3468(1)	18(1)
O(5)	-453(2)	-1195(1)	3485(1)	31(1)
O(6)	925(2)	1507(1)	2991(1)	24(1)
O(7)	-776(2)	287(1)	1403(1)	29(1)
C(1)	1919(3)	-4231(2)	1304(1)	30(1)
C(2)	5233(2)	-3147(2)	988(1)	25(1)
C(3)	4544(2)	-2404(2)	2875(1)	24(1)
C(4)	1192(2)	-1702(2)	1692(1)	21(1)
C(5)	1239(2)	-1907(2)	621(1)	24(1)
C(6)	3020(2)	-1351(2)	438(1)	23(1)
C(7)	4480(2)	-629(2)	1358(1)	20(1)
C(8)	3937(2)	338(1)	2112(1)	18(1)
C(9)	2029(2)	-331(1)	2359(1)	17(1)
C(10)	5296(2)	3157(1)	2552(1)	21(1)

C(11)	6422(2)	4213(2)	2256(1)	28(1)
C(12)	7576(3)	5299(2)	3010(2)	37(1)
C(13)	7646(3)	5328(2)	4055(2)	39(1)
C(14)	6542(3)	4279(2)	4352(1)	34(1)
C(15)	5339(2)	3196(2)	3603(1)	26(1)
C(16)	1246(2)	-871(2)	3932(1)	23(1)
C(17)	2126(3)	-935(2)	5046(1)	34(1)
C(18)	531(2)	498(2)	2183(1)	21(1)
C(19)	-248(3)	2445(2)	2814(2)	36(1)

Table 42Bond lengths [Å] and angles [°] for 455

Fe(1)-C(1)	1.7921(17)	Fe(1)-C(3)	1.7941(17)
Fe(1)-C(2)	1.7993(17)	Fe(1)-C(6)	2.0584(15)
Fe(1)-C(5)	2.0650(15)	Fe(1)-C(4)	2.0855(15)
Fe(1)-C(7)	2.0920(15)	S(1)-C(10)	1.7767(16)
S(1)-C(8)	1.8490(14)	O(1)-C(1)	1.144(2)
O(2)-C(2)	1.143(2)	O(3)-C(3)	1.145(2)
O(4)-C(16)	1.3562(18)	O(4)-C(9)	1.4586(17)
O(5)-C(16)	1.201(2)	O(6)-C(18)	1.3413(19)
O(6)-C(19)	1.4466(19)	O(7)-C(18)	1.1988(19)
C(4)-C(5)	1.426(2)	C(4)-C(9)	1.512(2)
C(4)-H(4)	0.978(5)	C(5)-C(6)	1.401(2)
C(5)-H(5)	0.978(5)	C(6)-C(7)	1.425(2)
C(6)-H(6)	0.978(5)	C(7)-C(8)	1.514(2)
C(7)-H(7)	0.977(5)	C(8)-C(9)	1.5527(19)
C(8)-H(8)	1.0000	C(9)-C(18)	1.535(2)
C(10)-C(15)	1.390(2)	C(10)-C(11)	1.396(2)
C(11)-C(12)	1.389(2)	C(11)-H(11)	0.9500
C(12)-C(13)	1.380(3)	C(12)-H(12)	0.9500
C(13)-C(14)	1.384(3)	C(13)-H(13)	0.9500
C(14)-C(15)	1.395(2)	C(14)-H(14)	0.9500
C(15)-H(15)	0.9500	C(16)-C(17)	1.494(2)
C(17)-H(17A)	0.9800	C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(1)-Fe(1)-C(3)	97.79(7)	C(1)-Fe(1)-C(2)	93.07(8)
C(3)-Fe(1)-C(2)	98.88(7)	C(1)-Fe(1)-C(6)	123.13(7)
C(3)-Fe(1)-C(6)	136.73(7)	C(2)-Fe(1)-C(6)	92.83(7)
C(1)-Fe(1)-C(5)	93.64(7)	C(3)-Fe(1)-C(5)	135.30(7)
C(2)-Fe(1)-C(5)	123.55(7)	C(6)-Fe(1)-C(5)	39.74(6)
C(1)-Fe(1)-C(4)	93.37(7)	C(3)-Fe(1)-C(4)	95.89(7)
C(2)-Fe(1)-C(4)	162.93(7)	C(6)-Fe(1)-C(4)	70.46(6)
C(5)-Fe(1)-C(4)	40.19(6)	C(1)-Fe(1)-C(7)	162.64(7)
C(3)-Fe(1)-C(7)	97.46(7)	C(2)-Fe(1)-C(7)	92.73(6)
C(6)-Fe(1)-C(7)	40.16(6)	C(5)-Fe(1)-C(7)	69.59(6)
C(4)-Fe(1)-C(7)	76.85(6)	C(10)-S(1)-C(8)	103.92(7)
C(16)-O(4)-C(9)	117.51(11)	C(18)-O(6)-C(19)	114.41(13)
O(1)-C(1)-Fe(1)	178.03(17)	O(2)-C(2)-Fe(1)	179.59(15)
O(3)-C(3)-Fe(1)	177.85(15)	C(5)-C(4)-C(9)	119.30(13)
C(5)-C(4)-Fe(1)	69.13(9)	C(9)-C(4)-Fe(1)	110.22(10)
C(5)-C(4)-H(4)	117.4(11)	C(9)-C(4)-H(4)	113.6(11)
Fe(1)-C(4)-H(4)	120.0(10)	C(6)-C(5)-C(4)	115.44(14)
C(6)-C(5)-Fe(1)	69.88(9)	C(4)-C(5)-Fe(1)	70.68(9)
C(6)-C(5)-H(5)	121.6(11)	C(4)-C(5)-H(5)	122.3(11)
Fe(1)-C(5)-H(5)	121.3(12)	C(5)-C(6)-C(7)	114.09(14)
C(5)-C(6)-Fe(1)	70.38(9)	C(7)-C(6)-Fe(1)	71.18(8)
C(5)-C(6)-H(6)	121.3(11)	C(7)-C(6)-H(6)	124.3(11)
Fe(1)-C(6)-H(6)	121.8(11)	C(6)-C(7)-C(8)	118.16(13)
C(6)-C(7)-Fe(1)	68.65(8)	C(8)-C(7)-Fe(1)	111.36(10)
C(6)-C(7)-H(7)	119.7(11)	C(8)-C(7)-H(7)	112.0(11)
Fe(1)-C(7)-H(7)	120.5(11)	C(7)-C(8)-C(9)	110.31(12)
C(7)-C(8)-S(1)	106.79(10)	C(9)-C(8)-S(1)	115.14(10)
C(7)-C(8)-H(8)	108.1	C(9)-C(8)-H(8)	108.1
S(1)-C(8)-H(8)	108.1	O(4)-C(9)-C(4)	111.35(11)
O(4)-C(9)-C(18)	109.79(11)	C(4)-C(9)-C(18)	110.18(12)
O(4)-C(9)-C(8)	103.73(11)	C(4)-C(9)-C(8)	109.89(12)

C(18)-C(9)-C(8)	111.76(11)	C(15)-C(10)-C(11)	119.78(15)
C(15)-C(10)-S(1)	124.13(12)	C(11)-C(10)-S(1)	116.09(12)
C(12)-C(11)-C(10)	119.95(17)	C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0	C(13)-C(12)-C(11)	120.30(17)
C(13)-C(12)-H(12)	119.8	C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	119.89(17)	C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1	C(13)-C(14)-C(15)	120.53(17)
C(13)-C(14)-H(14)	119.7	C(15)-C(14)-H(14)	119.7
C(10)-C(15)-C(14)	119.52(16)	C(10)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2	O(5)-C(16)-O(4)	123.20(14)
O(5)-C(16)-C(17)	126.16(15)	O(4)-C(16)-C(17)	110.64(14)
C(16)-C(17)-H(17A)	109.5	C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5	C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(17B)-C(17)-H(17C)	109.5
O(7)-C(18)-O(6)	124.98(14)	O(7)-C(18)-C(9)	123.65(14)
O(6)-C(18)-C(9)	111.32(12)	O(6)-C(19)-H(19A)	109.5
O(6)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
O(6)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 43 Anisotropic displacement parameters ($Å^2$ x 10^3) for 455. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	23(1)	16(1)	19(1)	4(1)	5(1)	4(1)
S(1)	24(1)	17(1)	21(1)	8(1)	7(1)	4(1)
O(1)	67(1)	24(1)	45(1)	5(1)	13(1)	-12(1)
O(2)	39(1)	33(1)	37(1)	9(1)	18(1)	17(1)
O(3)	43(1)	38(1)	23(1)	7(1)	4(1)	20(1)
O(4)	20(1)	21(1)	17(1)	7(1)	6(1)	6(1)
O(5)	26(1)	35(1)	34(1)	8(1)	15(1)	3(1)
O(6)	26(1)	24(1)	29(1)	9(1)	11(1)	14(1)
O(7)	20(1)	37(1)	30(1)	13(1)	3(1)	9(1)
C(1)	39(1)	26(1)	24(1)	5(1)	8(1)	5(1)
C(2)	33(1)	18(1)	24(1)	7(1)	5(1)	5(1)
C(3)	27(1)	18(1)	29(1)	7(1)	9(1)	9(1)
C(4)	17(1)	20(1)	23(1)	5(1)	5(1)	1(1)
C(5)	24(1)	24(1)	21(1)	4(1)	0(1)	7(1)
C(6)	31(1)	22(1)	21(1)	10(1)	10(1)	12(1)
C(7)	21(1)	18(1)	26(1)	10(1)	10(1)	6(1)
C(8)	17(1)	16(1)	21(1)	7(1)	6(1)	3(1)
C(9)	16(1)	19(1)	17(1)	6(1)	4(1)	4(1)
C(10)	20(1)	17(1)	28(1)	5(1)	7(1)	8(1)
C(11)	32(1)	19(1)	33(1)	9(1)	8(1)	5(1)
C(12)	39(1)	19(1)	47(1)	10(1)	5(1)	0(1)
C(13)	43(1)	23(1)	42(1)	-3(1)	-2(1)	6(1)
C(14)	38(1)	33(1)	29(1)	0(1)	5(1)	13(1)
C(15)	26(1)	25(1)	29(1)	6(1)	9(1)	8(1)
C(16)	29(1)	19(1)	25(1)	7(1)	14(1)	8(1)
C(17)	47(1)	39(1)	24(1)	12(1)	16(1)	14(1)
C(18)	17(1)	25(1)	25(1)	11(1)	9(1)	6(1)
C(19)	43(1)	37(1)	43(1)	18(1)	21(1)	28(1)

Table 44 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 455.

Atom	x	y	z	U(eq)
H(8)	4996	597	2781	21
H(11)	6400	4188	1539	33
H(12)	8320	6026	2805	44

H(13)	8451	6067	4569	47
H(14)	6604	4297	5073	40
H(15)	4554	2490	3808	31
H(17A)	2342	-69	5490	51
H(17B)	3367	-1170	5104	51
H(17C)	1245	-1605	5274	51
H(19A)	-80	2809	2193	54
H(19B)	156	3165	3426	54
H(19C)	-1616	1996	2703	54
H(4)	57(16)	-2206(15)	1862(14)	23(4)
H(5)	175(19)	-2508(15)	67(11)	31(5)
H(6)	3240(30)	-1539(19)	-254(7)	31(5)
H(7)	5815(12)	-317(17)	1323(15)	27(5)

Table 45 Dihedral angles [^{o}] for 455

Atom1 - Atom2 - Atom3 - Atom4	Dihedral
C(3) - Fe(1) - C(1) - O(1)	54(5)
C(2) - Fe(1) - C(1) - O(1)	154(5)
C(6) - Fe(1) - C(1) - O(1)	-111(5)
C(5) - Fe(1) - C(1) - O(1)	-82(5)
C(4) - Fe(1) - C(1) - O(1)	-42(5)
C(7) - Fe(1) - C(1) - O(1)	-97(5)
C(1) - Fe(1) - C(2) - O(2)	151(100)
C(3) - Fe(1) - C(2) - O(2)	-110(26)
C(6) - Fe(1) - C(2) - O(2)	28(26)
C(5) - Fe(1) - C(2) - O(2)	55(26)
C(4) - Fe(1) - C(2) - O(2)	39(26)
C(7) - Fe(1) - C(2) - O(2)	-12(26)
C(1) - Fe(1) - C(3) - O(3)	-14(4)
C(2) - Fe(1) - C(3) - O(3)	-108(4)
C(6) - Fe(1) - C(3) - O(3)	148(4)
C(5) - Fe(1) - C(3) - O(3)	89(4)
C(4) - Fe(1) - C(3) - O(3)	80(4)
C(7) - Fe(1) - C(3) - O(3)	158(4)
C(1) - Fe(1) - C(4) - C(5)	-91.66(10)
C(3) - Fe(1) - C(4) - C(5)	170.15(10)
C(2) - Fe(1) - C(4) - C(5)	20.3(3)
C(6) - Fe(1) - C(4) - C(5)	32.41(9)
C(7) - Fe(1) - C(4) - C(5)	73.83(9)
C(1) - Fe(1) - C(4) - C(9)	153.66(11)
C(3) - Fe(1) - C(4) - C(9)	55.46(11)
C(2) - Fe(1) - C(4) - C(9)	-94.4(2)
C(6) - Fe(1) - C(4) - C(9)	-82.28(11)
C(5) - Fe(1) - C(4) - C(9)	-114.69(14)
C(7) - Fe(1) - C(4) - C(9)	-40.85(10)
C(9) - C(4) - C(5) - C(6)	46.9(2)
Fe(1) - C(4) - C(5) - C(6)	-55.22(12)
C(9) - C(4) - C(5) - Fe(1)	102.14(13)
C(1) - Fe(1) - C(5) - C(6)	-141.27(10)
C(3) - Fe(1) - C(5) - C(6)	113.81(12)
C(2) - Fe(1) - C(5) - C(6)	-45.16(12)
C(4) - Fe(1) - C(5) - C(6)	127.82(13)
C(7) - Fe(1) - C(5) - C(6)	34.13(9)
C(1) - Fe(1) - C(5) - C(4)	90.91(10)
C(3) - Fe(1) - C(5) - C(4)	-14.01(14)
C(2) - Fe(1) - C(5) - C(4)	-172.97(9)
C(6) - Fe(1) - C(5) - C(4)	-127.82(13)
C(7) - Fe(1) - C(5) - C(4)	-93.69(10)
C(4) - C(5) - C(6) - C(7)	-2.1(2)
Fe(1) - C(5) - C(6) - C(7)	-57.70(11)
C(4) - C(5) - C(6) - Fe(1)	55.64(12)
C(1) - Fe(1) - C(6) - C(5)	48.21(12)
C(3) - Fe(1) - C(6) - C(5)	-110.14(12)
C(2) - Fe(1) - C(6) - C(5)	143.73(10)
C(4) - Fe(1) - C(6) - C(5)	-32.75(9)
C(7) - Fe(1) - C(6) - C(5)	-125.40(13)
C(1) - Fe(1) - C(6) - C(7)	173.60(10)

C(3) - Fe(1) - C(6) - C(7)	15.26(14)
C(2) - Fe(1) - C(6) - C(7)	-90.88(10)
C(5) - Fe(1) - C(6) - C(7)	125.40(13)
C(4) - Fe(1) - C(6) - C(7)	92.65(9)
C(5) - C(6) - C(7) - C(8)	-46.29(19)
Fe(1) - C(6) - C(7) - C(8)	-103.55(12)
C(5) - C(6) - C(7) - Fe(1)	57.26(12)
C(1) - Fe(1) - C(7) - C(6)	-18.2(3)
C(3) - Fe(1) - C(7) - C(6)	-169.52(10)
C(2) - Fe(1) - C(7) - C(6)	91.16(10)
C(5) - Fe(1) - C(7) - C(6)	-33.78(9)
C(4) - Fe(1) - C(7) - C(6)	-75.18(9)
C(1) - Fe(1) - C(7) - C(8)	94.8(3)
C(3) - Fe(1) - C(7) - C(8)	-56.49(11)
C(2) - Fe(1) - C(7) - C(8)	-155.81(11)
C(6) - Fe(1) - C(7) - C(8)	113.03(14)
C(5) - Fe(1) - C(7) - C(8)	79.25(11)
C(4) - Fe(1) - C(7) - C(8)	37.85(10)
C(6) - C(7) - C(8) - C(9)	48.82(17)
Fe(1) - C(7) - C(8) - C(9)	-27.65(14)
C(6) - C(7) - C(8) - S(1)	-76.97(14)
Fe(1) - C(7) - C(8) - S(1)	-153.43(7)
C(10) - S(1) - C(8) - C(7)	-130.01(10)
C(10) - S(1) - C(8) - C(9)	107.17(11)
C(16) - O(4) - C(9) - C(4)	-65.21(15)
C(16) - O(4) - C(9) - C(18)	57.08(16)
C(16) - O(4) - C(9) - C(8)	176.66(11)
C(5) - C(4) - C(9) - O(4)	-154.89(13)
Fe(1) - C(4) - C(9) - O(4)	-78.10(12)
C(5) - C(4) - C(9) - C(18)	83.05(16)
Fe(1) - C(4) - C(9) - C(18)	159.83(9)
C(5) - C(4) - C(9) - C(8)	-40.53(18)
Fe(1) - C(4) - C(9) - C(8)	36.26(14)
C(7) - C(8) - C(9) - O(4)	113.74(12)
S(1) - C(8) - C(9) - O(4)	-125.34(10)
C(7) - C(8) - C(9) - C(4)	-5.40(16)
S(1) - C(8) - C(9) - C(4)	115.52(12)
C(7) - C(8) - C(9) - C(18)	-128.04(13)
S(1) - C(8) - C(9) - C(18)	-7.12(16)
C(8) - S(1) - C(10) - C(15)	-36.68(15)
C(8) - S(1) - C(10) - C(11)	143.69(12)
C(15) - C(10) - C(11) - C(12)	-0.2(2)
S(1) - C(10) - C(11) - C(12)	179.43(13)
C(10) - C(11) - C(12) - C(13)	1.4(3)
C(11) - C(12) - C(13) - C(14)	-0.9(3)
C(12) - C(13) - C(14) - C(15)	-0.7(3)
C(11) - C(10) - C(15) - C(14)	-1.4(2)
S(1) - C(10) - C(15) - C(14)	179.00(12)
C(13) - C(14) - C(15) - C(10)	1.9(3)
C(9) - O(4) - C(16) - O(5)	-3.3(2)
C(9) - O(4) - C(16) - C(17)	176.75(13)
C(19) - O(6) - C(18) - O(7)	-6.3(2)
C(19) - O(6) - C(18) - C(9)	171.21(13)
O(4) - C(9) - C(18) - O(7)	-147.12(14)
C(4) - C(9) - C(18) - O(7)	-24.1(2)
C(8) - C(9) - C(18) - O(7)	98.34(17)
O(4) - C(9) - C(18) - O(6)	35.38(16)
C(4) - C(9) - C(18) - O(6)	158.36(12)
C(8) - C(9) - C(18) - O(6)	-79.16(15)

Symmetry transformations used to generate equivalent atoms:

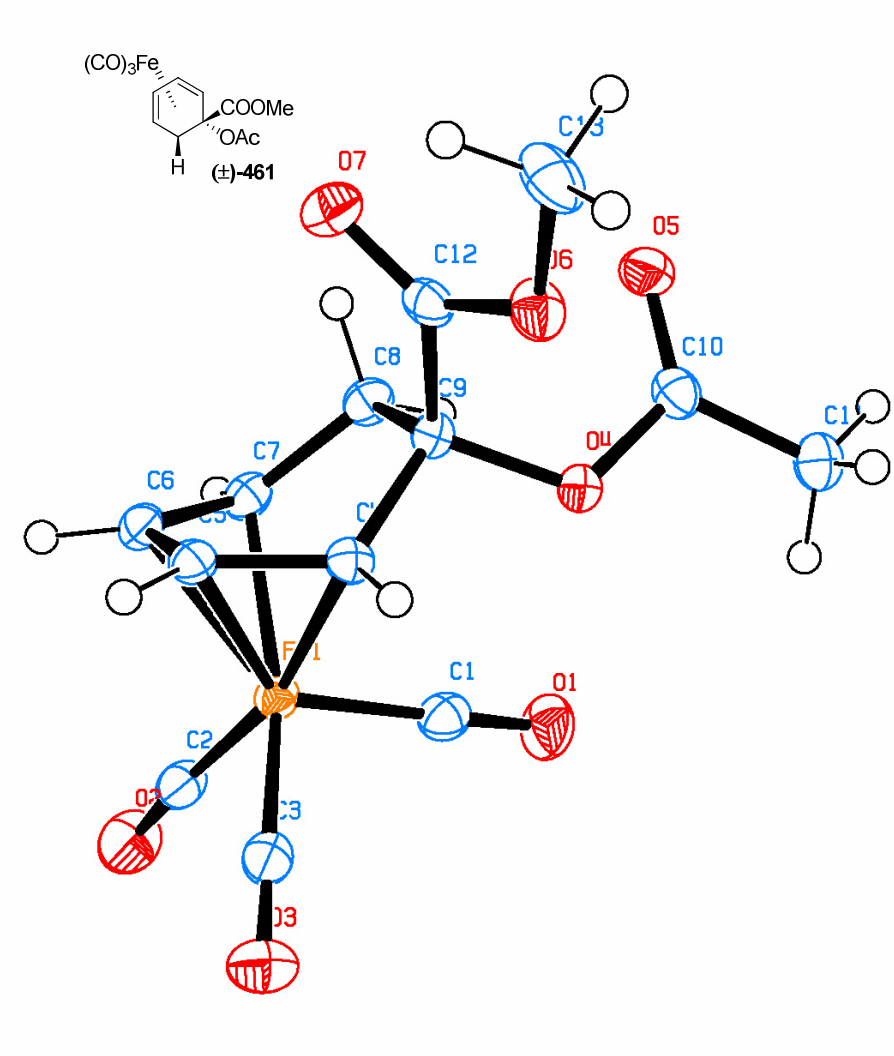


Figure 28 ORTEP diagram (50% probability factor for thermal ellipsoid) with atomic numbering scheme for **461**

Table 46 Crystal data and structure refinement for 461

Identification code	k09sel5
Empirical formula	C13 H12 Fe O7
Formula weight	336.08
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.9550(2)Å α = 90°
	b = 5.9360(1)Å β = 91.773(1)°
	c = 22.9660(5)Å γ = 90°
Volume	1356.48(5) $Å^3$
Z	4
Density (calculated)	1.646 Mg/m^3

Absorption coefficient	1.143 mm^{-1}
F(000)	688
Crystal size	0.25 x 0.20 x 0.20 mm
Theta range for data collection	3.55 to 27.48°
Index ranges	-12<=h<=12; -7<=k<=7; -29<=l<=29
Reflections collected	23752
Independent reflections	3095 [R(int) = 0.0469]
Reflections observed (>2σ)	2590
Data Completeness	0.996
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.801 and 0.750
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3095 / 4 / 209
Goodness-of-fit on F^2	1.092
Final R indices [I>2σ(I)]	R1 = 0.0293 wR2 = 0.0685
R indices (all data)	R1 = 0.0420 wR2 = 0.0734
Largest diff. peak and hole	0.519 and -0.613 $eÅ^{-3}$

Notes:

H4-7 located and refined at distances of 0.98Å from the relevant carbon parent.

This structure is a racemate.

Table 47 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 461. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe(1)	8212(1)	-80(1)	1054(1)	19(1)
O(1)	6545(1)	1514(2)	63(1)	36(1)
O(2)	10159(2)	-2547(2)	357(1)	40(1)
O(3)	10160(1)	3616(2)	1182(1)	33(1)
O(4)	4918(1)	2004(2)	1166(1)	21(1)
O(5)	2897(1)	342(2)	1244(1)	28(1)
O(6)	4343(1)	2488(2)	2262(1)	27(1)
O(7)	4780(1)	-1146(2)	2480(1)	29(1)
C(1)	7201(2)	906(3)	448(1)	25(1)
C(2)	9409(2)	-1644(3)	642(1)	26(1)
C(3)	9404(2)	2184(3)	1137(1)	24(1)
C(4)	6937(2)	1173(3)	1682(1)	19(1)
C(5)	7912(2)	-338(3)	1931(1)	20(1)
C(6)	7918(2)	-2500(3)	1679(1)	22(1)
C(7)	6937(2)	-2827(3)	1222(1)	22(1)
C(8)	5513(2)	-2010(3)	1296(1)	22(1)
C(9)	5506(2)	350(3)	1565(1)	19(1)
C(10)	3585(2)	1795(3)	1039(1)	23(1)
C(11)	3128(2)	3600(3)	625(1)	31(1)
C(12)	4804(2)	425(3)	2150(1)	21(1)
C(13)	3625(2)	2794(4)	2797(1)	34(1)

Table 48 Bond lengths [Å] and angles [°] for 461

Fe(1)-C(1)	1.7889(18)	Fe(1)-C(3)	1.7990(18)
Fe(1)-C(2)	1.8025(18)	Fe(1)-C(5)	2.0527(16)
Fe(1)-C(6)	2.0594(16)	Fe(1)-C(4)	2.0872(16)
Fe(1)-C(7)	2.1096(16)	O(1)-C(1)	1.143(2)

O(2)-C(2)	1.141(2)	O(3)-C(3)	1.138(2)
O(4)-C(10)	1.356(2)	O(4)-C(9)	1.4535(19)
O(5)-C(10)	1.206(2)	O(6)-C(12)	1.336(2)
O(6)-C(13)	1.453(2)	O(7)-C(12)	1.203(2)
C(4)-C(5)	1.429(2)	C(4)-C(9)	1.522(2)
C(4)-H(4)	0.979(5)	C(5)-C(6)	1.408(2)
C(5)-H(5)	0.979(5)	C(6)-C(7)	1.425(2)
C(6)-H(6)	0.976(5)	C(7)-C(8)	1.513(2)
C(7)-H(7)	0.980(5)	C(8)-C(9)	1.532(2)
C(8)-H(8A)	0.9900	C(8)-H(8B)	0.9900
C(9)-C(12)	1.534(2)	C(10)-C(11)	1.495(2)
C(11)-H(11A)	0.9800	C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(1)-Fe(1)-C(3)	101.05(8)	C(1)-Fe(1)-C(2)	97.21(8)
C(3)-Fe(1)-C(2)	89.75(8)	C(1)-Fe(1)-C(5)	133.80(7)
C(3)-Fe(1)-C(5)	93.85(7)	C(2)-Fe(1)-C(5)	126.57(7)
C(1)-Fe(1)-C(6)	132.97(7)	C(3)-Fe(1)-C(6)	123.68(7)
C(2)-Fe(1)-C(6)	96.75(7)	C(5)-Fe(1)-C(6)	40.05(7)
C(1)-Fe(1)-C(4)	94.65(7)	C(3)-Fe(1)-C(4)	94.25(7)
C(2)-Fe(1)-C(4)	166.53(7)	C(5)-Fe(1)-C(4)	40.37(6)
C(6)-Fe(1)-C(4)	70.36(6)	C(1)-Fe(1)-C(7)	93.90(7)
C(3)-Fe(1)-C(7)	163.07(7)	C(2)-Fe(1)-C(7)	96.27(7)
C(5)-Fe(1)-C(7)	69.86(7)	C(6)-Fe(1)-C(7)	39.96(7)
C(4)-Fe(1)-C(7)	76.51(6)	C(10)-O(4)-C(9)	116.52(12)
C(12)-O(6)-C(13)	117.25(14)	O(1)-C(1)-Fe(1)	179.17(17)
O(2)-C(2)-Fe(1)	176.20(16)	O(3)-C(3)-Fe(1)	179.10(15)
C(5)-C(4)-C(9)	119.31(14)	C(5)-C(4)-Fe(1)	68.51(9)
C(9)-C(4)-Fe(1)	110.48(11)	C(5)-C(4)-H(4)	116.1(10)
C(9)-C(4)-H(4)	113.8(10)	Fe(1)-C(4)-H(4)	121.4(10)
C(6)-C(5)-C(4)	114.73(15)	C(6)-C(5)-Fe(1)	70.24(10)
C(4)-C(5)-Fe(1)	71.11(9)	C(6)-C(5)-H(5)	120.6(11)
C(4)-C(5)-H(5)	124.2(10)	Fe(1)-C(5)-H(5)	121.7(12)
C(5)-C(6)-C(7)	114.57(15)	C(5)-C(6)-Fe(1)	69.72(9)
C(7)-C(6)-Fe(1)	71.92(10)	C(5)-C(6)-H(6)	120.7(11)
C(7)-C(6)-H(6)	124.3(11)	Fe(1)-C(6)-H(6)	120.8(11)
C(6)-C(7)-C(8)	119.81(15)	C(6)-C(7)-Fe(1)	68.13(9)
C(8)-C(7)-Fe(1)	110.12(11)	C(6)-C(7)-H(7)	116.0(11)
C(8)-C(7)-H(7)	116.1(11)	Fe(1)-C(7)-H(7)	117.8(11)
C(7)-C(8)-C(9)	110.73(13)	C(7)-C(8)-H(8A)	109.5
C(9)-C(8)-H(8A)	109.5	C(7)-C(8)-H(8B)	109.5
C(9)-C(8)-H(8B)	109.5	H(8A)-C(8)-H(8B)	108.1
O(4)-C(9)-C(4)	104.50(12)	O(4)-C(9)-C(8)	111.73(13)
C(4)-C(9)-C(8)	110.44(13)	O(4)-C(9)-C(12)	110.27(13)
C(4)-C(9)-C(12)	106.63(13)	C(8)-C(9)-C(12)	112.83(13)
O(5)-C(10)-O(4)	123.06(15)	O(5)-C(10)-C(11)	126.56(16)
O(4)-C(10)-C(11)	110.38(14)	C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	O(7)-C(12)-O(6)	125.18(16)
O(7)-C(12)-C(9)	123.26(15)	O(6)-C(12)-C(9)	111.30(14)
O(6)-C(13)-H(13A)	109.5	O(6)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5	O(6)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(13B)-C(13)-H(13C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 49 Anisotropic displacement parameters ($Å^2$ x 10^3) for 461. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Fe(1)	21(1)	18(1)	17(1)	1(1)	2(1)	1(1)
O(1)	40(1)	46(1)	23(1)	7(1)	-3(1)	8(1)
O(2)	48(1)	36(1)	37(1)	1(1)	18(1)	13(1)

O(3)	33(1)	30(1)	36(1)	-3(1)	8(1)	-7(1)
O(4)	19(1)	21(1)	22(1)	3(1)	-1(1)	1(1)
O(5)	21(1)	35(1)	29(1)	5(1)	1(1)	-3(1)
O(6)	28(1)	31(1)	21(1)	-3(1)	3(1)	8(1)
O(7)	34(1)	31(1)	24(1)	5(1)	4(1)	-2(1)
C(1)	28(1)	24(1)	24(1)	0(1)	7(1)	1(1)
C(2)	30(1)	23(1)	25(1)	5(1)	4(1)	0(1)
C(3)	26(1)	25(1)	21(1)	1(1)	6(1)	6(1)
C(4)	19(1)	19(1)	19(1)	-1(1)	2(1)	0(1)
C(5)	19(1)	25(1)	16(1)	3(1)	2(1)	-1(1)
C(6)	23(1)	22(1)	21(1)	5(1)	3(1)	3(1)
C(7)	27(1)	17(1)	21(1)	1(1)	2(1)	1(1)
C(8)	25(1)	18(1)	22(1)	-1(1)	1(1)	-2(1)
C(9)	19(1)	20(1)	18(1)	3(1)	-1(1)	1(1)
C(10)	21(1)	28(1)	21(1)	-1(1)	0(1)	3(1)
C(11)	25(1)	35(1)	32(1)	8(1)	-5(1)	3(1)
C(12)	15(1)	27(1)	21(1)	-1(1)	-2(1)	-2(1)
C(13)	25(1)	50(1)	26(1)	-8(1)	4(1)	10(1)

Table 50 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 461.

Atom	x	y	z	U(eq)
H(8A)	5033	-3068	1550	26
H(8B)	5034	-1977	911	26
H(11A)	2274	3155	435	46
H(11B)	3806	3820	330	46
H(11C)	3004	5010	839	46
H(13A)	2688	2321	2736	50
H(13B)	3652	4386	2910	50
H(13C)	4049	1881	3107	50
H(4)	6994(17)	2740(12)	1813(7)	16(4)
H(5)	8607(14)	100(30)	2220(7)	22(5)
H(6)	8625(13)	-3580(20)	1783(8)	24(5)
H(7)	7038(19)	-4190(20)	987(7)	26(5)

Table 51 Dihedral angles [^{o}] for 461

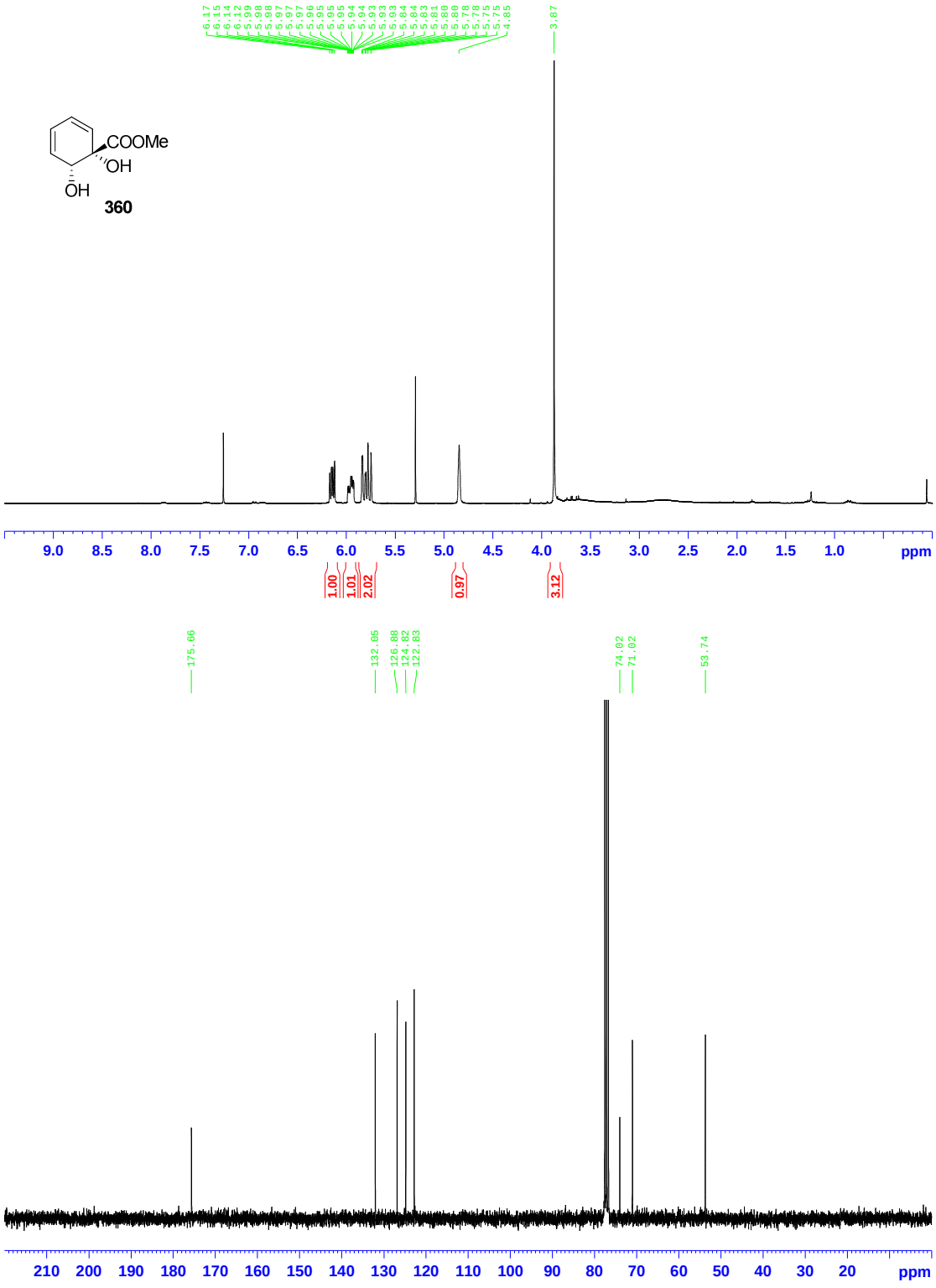
Atom1 - Atom2 - Atom3 - Atom4	Dihedral
C(3) - Fe(1) - C(1) - O(1)	-171(100)
C(2) - Fe(1) - C(1) - O(1)	97(12)
C(5) - Fe(1) - C(1) - O(1)	-65(12)
C(6) - Fe(1) - C(1) - O(1)	-9(12)
C(4) - Fe(1) - C(1) - O(1)	-76(12)
C(7) - Fe(1) - C(1) - O(1)	1(12)
C(1) - Fe(1) - C(2) - O(2)	34(3)
C(3) - Fe(1) - C(2) - O(2)	-67(3)
C(5) - Fe(1) - C(2) - O(2)	-162(3)
C(6) - Fe(1) - C(2) - O(2)	169(3)
C(4) - Fe(1) - C(2) - O(2)	-175(2)
C(7) - Fe(1) - C(2) - O(2)	129(3)
C(1) - Fe(1) - C(3) - O(3)	-42(10)
C(2) - Fe(1) - C(3) - O(3)	55(10)
C(5) - Fe(1) - C(3) - O(3)	-178(100)
C(6) - Fe(1) - C(3) - O(3)	153(10)
C(4) - Fe(1) - C(3) - O(3)	-138(10)
C(7) - Fe(1) - C(3) - O(3)	166(10)
C(1) - Fe(1) - C(4) - C(5)	167.57(10)
C(3) - Fe(1) - C(4) - C(5)	-90.95(10)
C(2) - Fe(1) - C(4) - C(5)	16.0(3)
C(6) - Fe(1) - C(4) - C(5)	33.38(10)
C(7) - Fe(1) - C(4) - C(5)	74.67(10)
C(1) - Fe(1) - C(4) - C(9)	53.08(12)
C(3) - Fe(1) - C(4) - C(9)	154.56(11)

C(2) - Fe(1) - C(4) - C(9)	-98.5(3)
C(5) - Fe(1) - C(4) - C(9)	-114.49(15)
C(6) - Fe(1) - C(4) - C(9)	-81.11(11)
C(7) - Fe(1) - C(4) - C(9)	-39.82(11)
C(9) - C(4) - C(5) - C(6)	45.6(2)
Fe(1) - C(4) - C(5) - C(6)	-56.56(13)
C(9) - C(4) - C(5) - Fe(1)	102.13(14)
C(1) - Fe(1) - C(5) - C(6)	109.07(12)
C(3) - Fe(1) - C(5) - C(6)	-141.62(11)
C(2) - Fe(1) - C(5) - C(6)	-49.07(13)
C(4) - Fe(1) - C(5) - C(6)	126.36(14)
C(7) - Fe(1) - C(5) - C(6)	33.63(10)
C(1) - Fe(1) - C(5) - C(4)	-17.29(14)
C(3) - Fe(1) - C(5) - C(4)	92.03(10)
C(2) - Fe(1) - C(5) - C(4)	-175.42(10)
C(6) - Fe(1) - C(5) - C(4)	-126.36(14)
C(7) - Fe(1) - C(5) - C(4)	-92.73(10)
C(4) - C(5) - C(6) - C(7)	-0.8(2)
Fe(1) - C(5) - C(6) - C(7)	-57.80(13)
C(4) - C(5) - C(6) - Fe(1)	57.03(12)
C(1) - Fe(1) - C(6) - C(5)	-111.22(12)
C(3) - Fe(1) - C(6) - C(5)	48.12(13)
C(2) - Fe(1) - C(6) - C(5)	142.34(11)
C(4) - Fe(1) - C(6) - C(5)	-33.64(10)
C(7) - Fe(1) - C(6) - C(5)	-125.94(14)
C(1) - Fe(1) - C(6) - C(7)	14.72(14)
C(3) - Fe(1) - C(6) - C(7)	174.06(10)
C(2) - Fe(1) - C(6) - C(7)	-91.72(11)
C(5) - Fe(1) - C(6) - C(7)	125.94(14)
C(4) - Fe(1) - C(6) - C(7)	92.31(10)
C(5) - C(6) - C(7) - C(8)	-44.8(2)
Fe(1) - C(6) - C(7) - C(8)	-101.38(14)
C(5) - C(6) - C(7) - Fe(1)	56.61(13)
C(1) - Fe(1) - C(7) - C(6)	-169.26(10)
C(3) - Fe(1) - C(7) - C(6)	-17.2(3)
C(2) - Fe(1) - C(7) - C(6)	93.04(11)
C(5) - Fe(1) - C(7) - C(6)	-33.70(10)
C(4) - Fe(1) - C(7) - C(6)	-75.41(10)
C(1) - Fe(1) - C(7) - C(8)	-54.21(12)
C(3) - Fe(1) - C(7) - C(8)	97.9(3)
C(2) - Fe(1) - C(7) - C(8)	-151.92(12)
C(5) - Fe(1) - C(7) - C(8)	81.35(12)
C(6) - Fe(1) - C(7) - C(8)	115.05(16)
C(4) - Fe(1) - C(7) - C(8)	39.64(11)
C(6) - C(7) - C(8) - C(9)	43.7(2)
Fe(1) - C(7) - C(8) - C(9)	-32.00(16)
C(10) - O(4) - C(9) - C(4)	-173.19(13)
C(10) - O(4) - C(9) - C(8)	67.37(18)
C(10) - O(4) - C(9) - C(12)	-58.95(17)
C(5) - C(4) - C(9) - O(4)	-163.64(14)
Fe(1) - C(4) - C(9) - O(4)	-87.45(12)
C(5) - C(4) - C(9) - C(8)	-43.3(2)
Fe(1) - C(4) - C(9) - C(8)	32.84(15)
C(5) - C(4) - C(9) - C(12)	79.58(18)
Fe(1) - C(4) - C(9) - C(12)	155.76(10)
C(7) - C(8) - C(9) - O(4)	115.63(15)
C(7) - C(8) - C(9) - C(4)	-0.23(18)
C(7) - C(8) - C(9) - C(12)	-119.46(15)
C(9) - O(4) - C(10) - O(5)	0.7(2)
C(9) - O(4) - C(10) - C(11)	-179.80(14)
C(13) - O(6) - C(12) - O(7)	-7.1(2)
C(13) - O(6) - C(12) - C(9)	178.59(13)
O(4) - C(9) - C(12) - O(7)	155.84(15)
C(4) - C(9) - C(12) - O(7)	-91.28(18)
C(8) - C(9) - C(12) - O(7)	30.1(2)
O(4) - C(9) - C(12) - O(6)	-29.76(18)
C(4) - C(9) - C(12) - O(6)	83.12(16)
C(8) - C(9) - C(12) - O(6)	-155.46(13)

Symmetry transformations used to generate equivalent atoms:

Appendix 2

^{1}H, ^{13}C NMR Spectra of new compounds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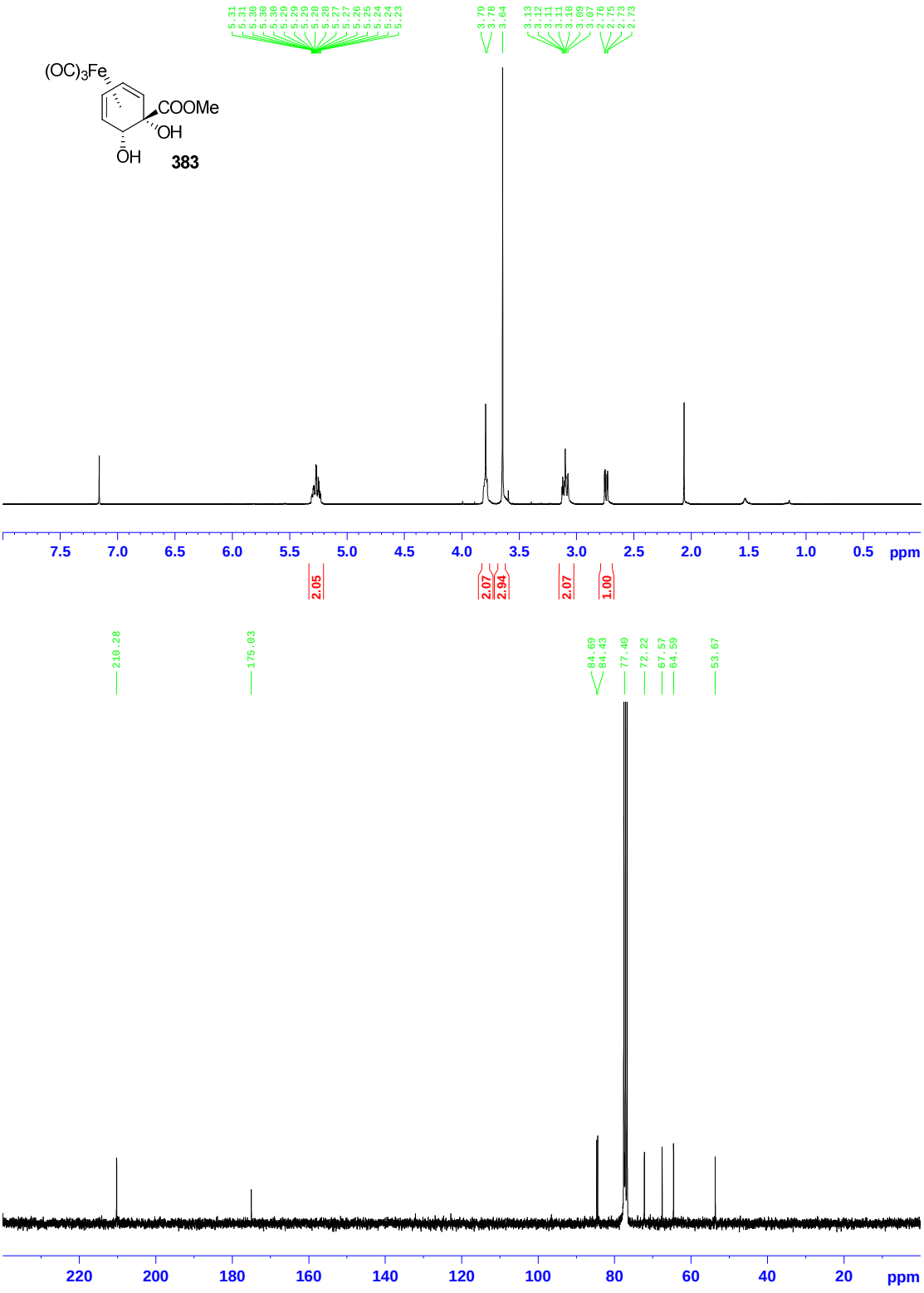
6.15
6.14
6.12
5.99
5.98
5.97
5.97
5.96
5.95
5.95
5.95
5.94
5.93
5.93
5.93
5.84
5.83
5.81
5.80
5.78
5.75
5.75
4.85
3.87
COOMe
OH
OH
360
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
2.02
0.97
3.12
175.66
132.05
126.88
124.82
122.83
74.02
71.02
53.74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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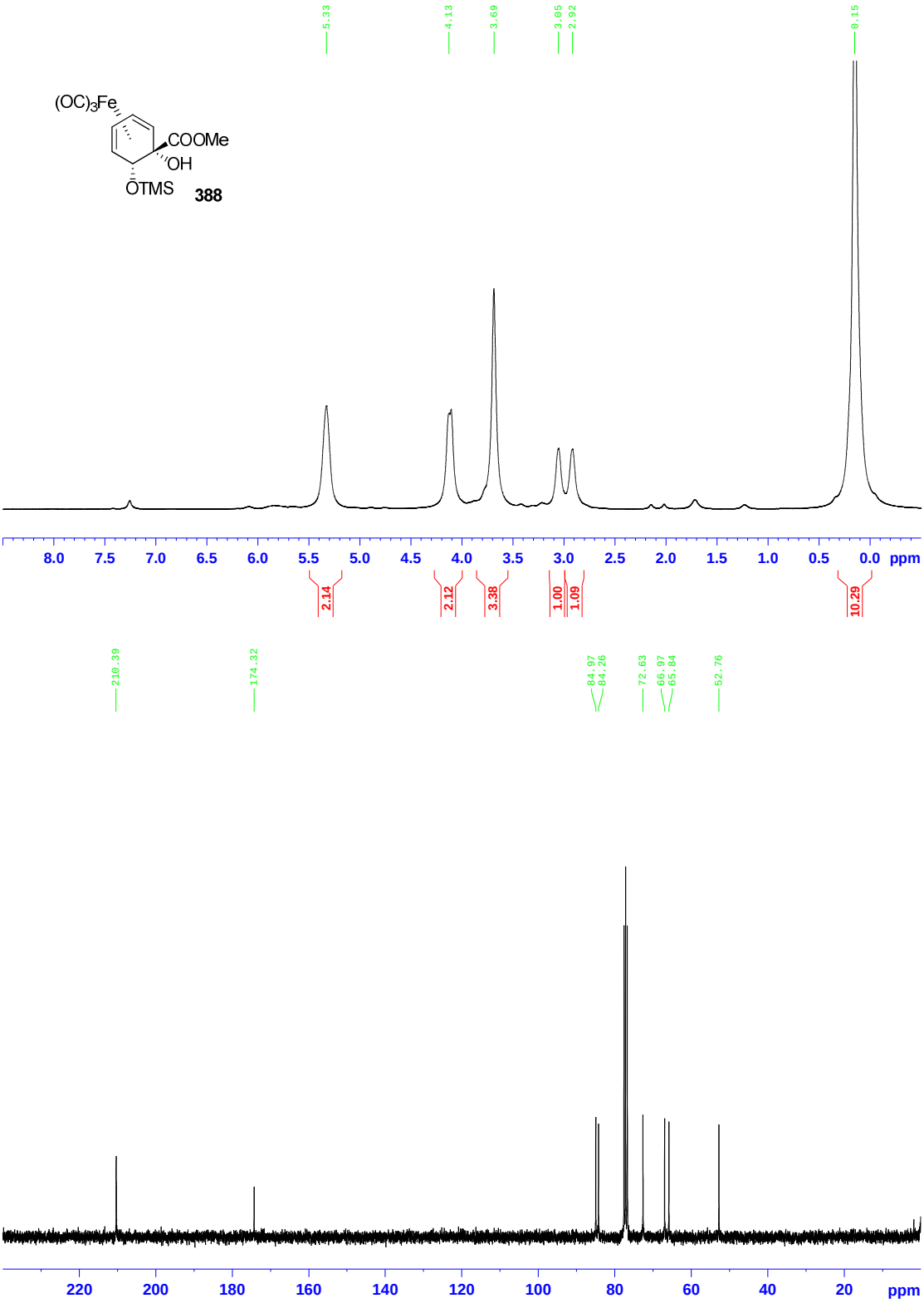
COOMe
OH
OH
383
5.31
5.31
5.30
5.30
5.30
5.29
5.29
5.29
5.28
5.28
5.27
5.27
5.26
5.25
5.24
5.24
5.23
3.79
3.78
3.64
3.13
3.12
3.11
3.11
3.10
3.09
3.07
2.76
2.75
2.73
2.73
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05
2.07
2.94
2.07
1.00
210.28
175.03
84.69
84.43
77.40
72.22
67.57
64.59
53.67
220 200 180 160 140 120 100 80 60 40 20 ppm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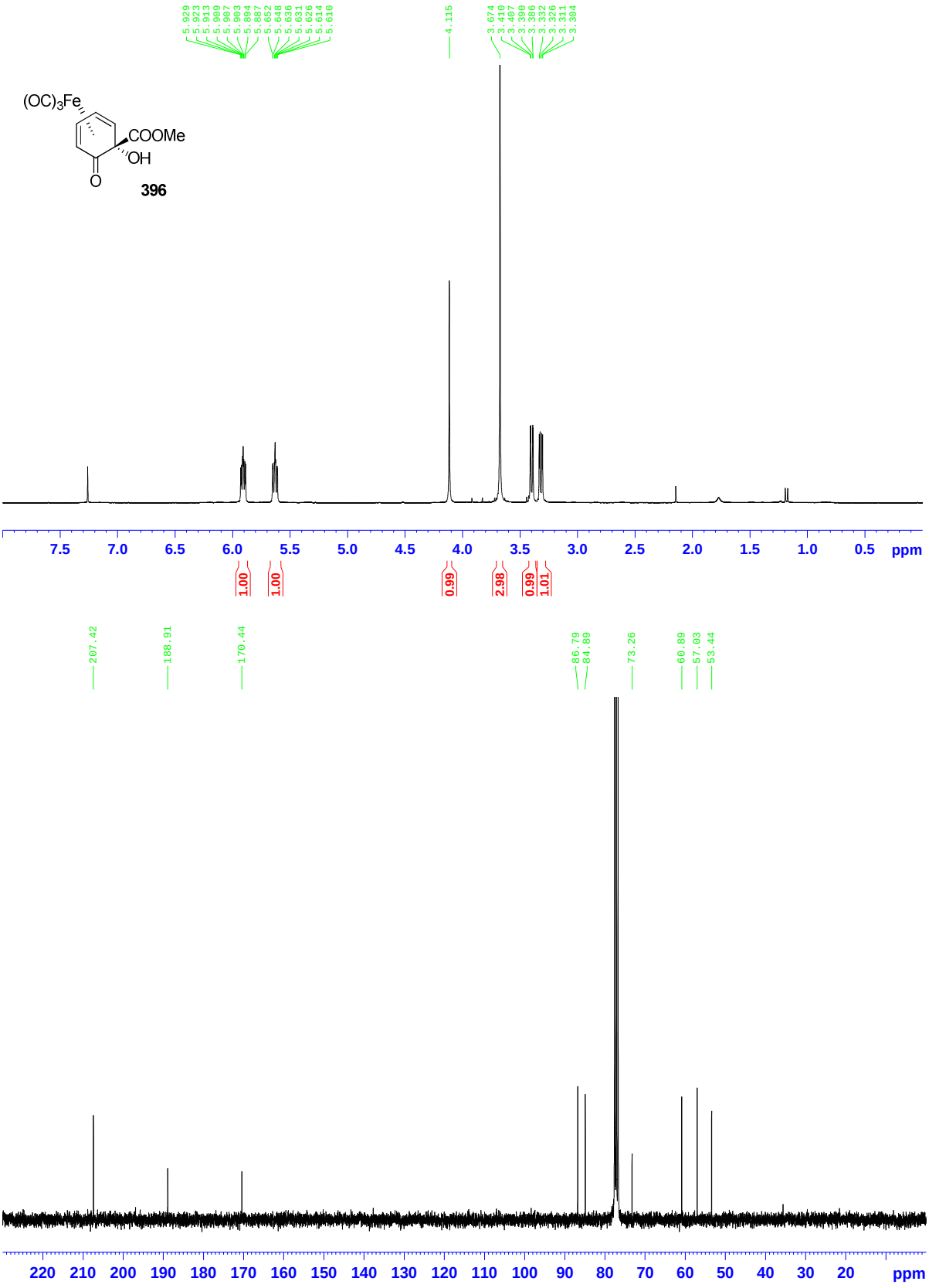
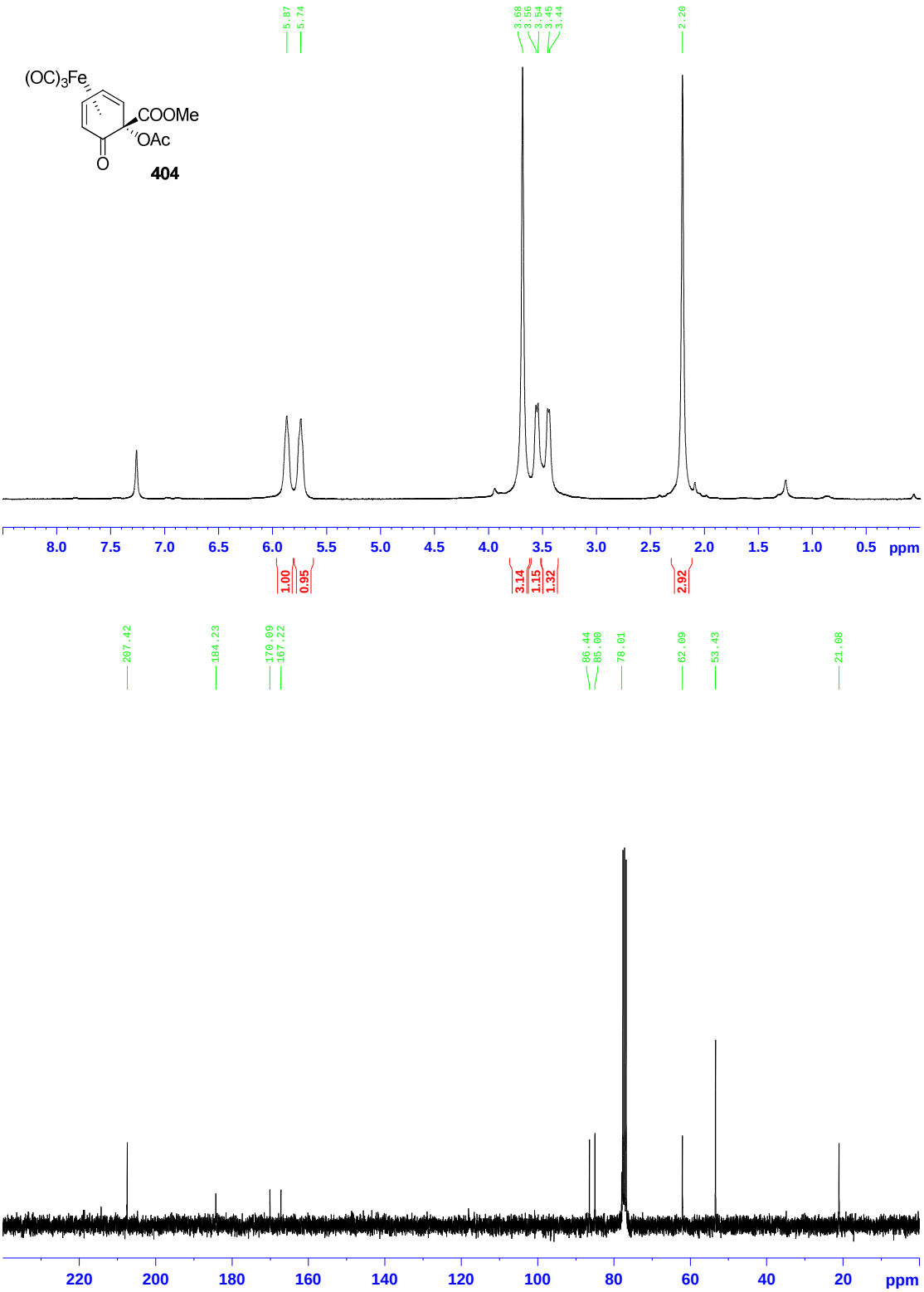
COOMe
OH
OTMS
388
5.33
4.13
3.69
3.05
2.92
0.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.14
2.12
3.38
1.00
1.09
10.29
210.39
174.32
84.97
84.26
72.63
66.97
65.84
52.76
220 200 180 160 140 120 100 80 60 40 20 ppm


5.929
5.923
5.913
5.909
5.907
5.903
5.894
5.887
5.652
5.648
5.636
5.631
5.626
5.614
5.610
4.115
3.674
3.410
3.407
3.390
3.386
3.332
3.326
3.311
3.304
(OC)3Fe
COOMe
OH
O
396
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.00
0.99
2.98
0.99
1.01
207.42
188.91
170.44
86.79
84.89
73.26
60.89
57.03
53.44
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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COOMe
OAc
O
404
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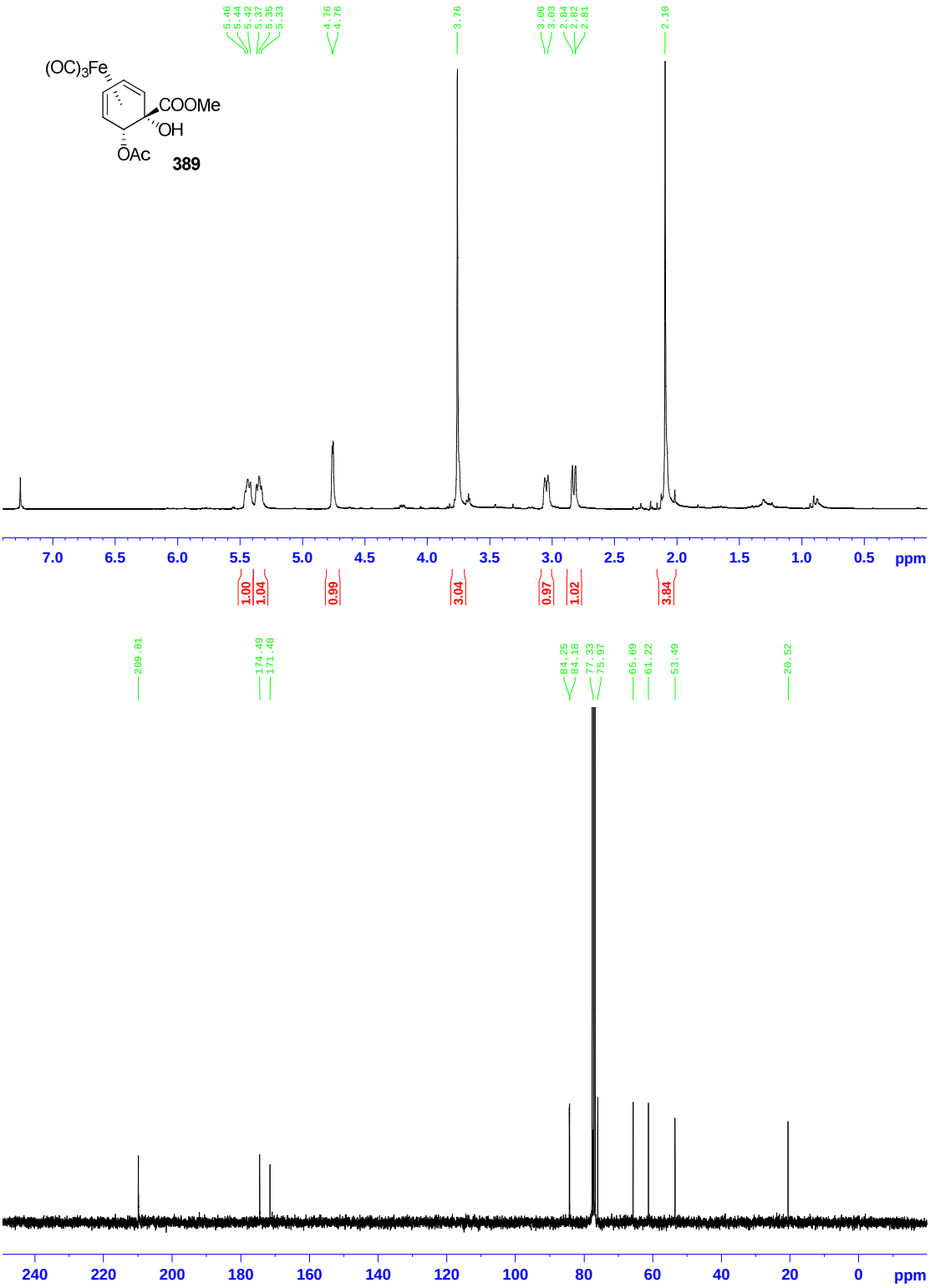
5.74
3.68
3.56
3.54
3.45
3.44
2.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.95
3.14
1.15
1.32
2.92
207.42
184.23
170.09
167.22
86.44
85.00
78.01
62.09
53.43
21.08
220
200
180
160
140
120
100
80
60
40
20
ppm


(OC)3Fe
COOMe
OH
OAc
389
5.46
5.44
5.42
5.37
5.35
5.33
4.76
4.76
3.76
3.06
3.03
2.84
2.82
2.81
2.10
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
0.99
3.04
0.97
1.02
3.84
209.81
174.49
171.48
84.25
84.18
77.33
75.97
65.69
61.22
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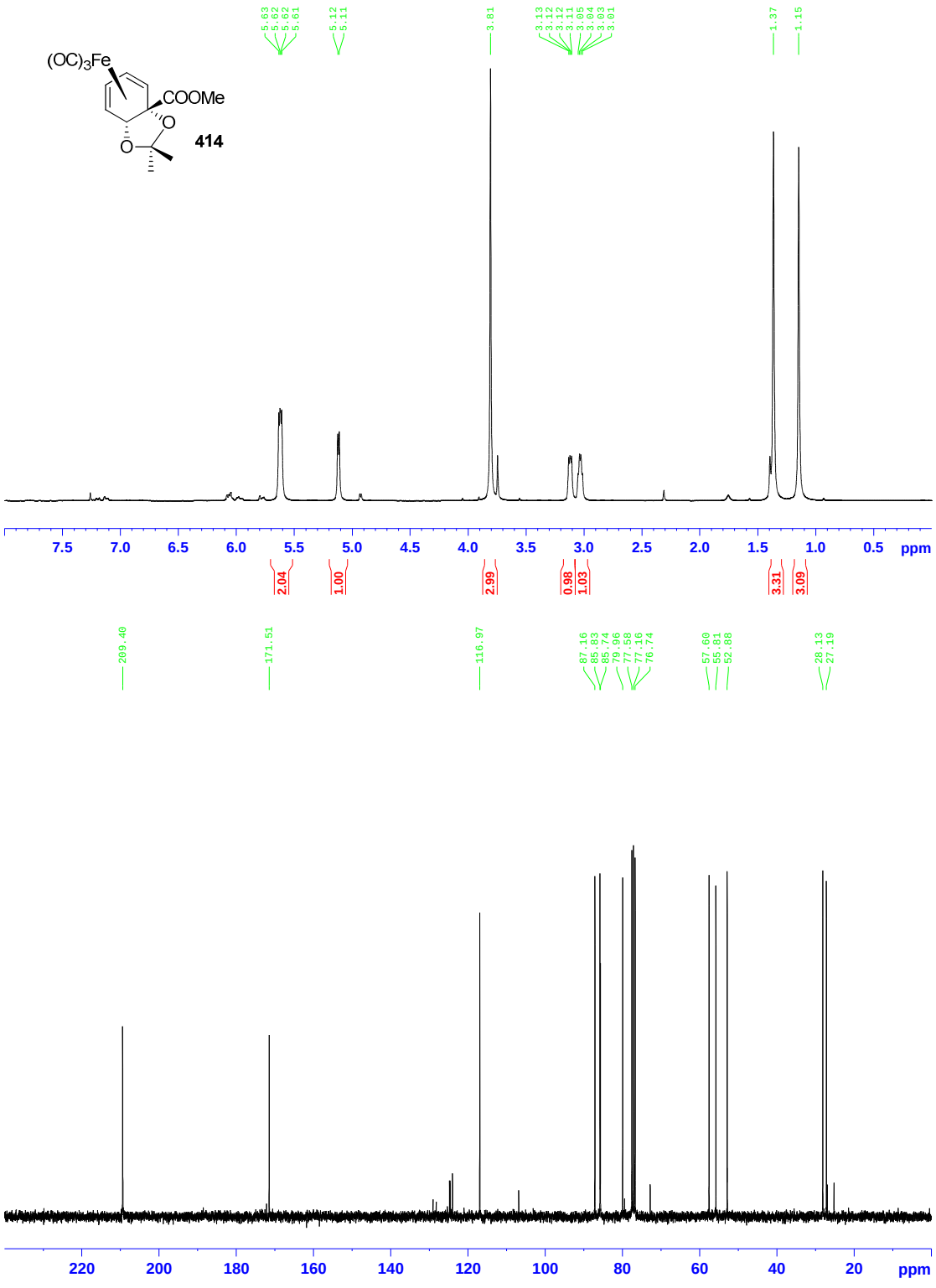
20.52
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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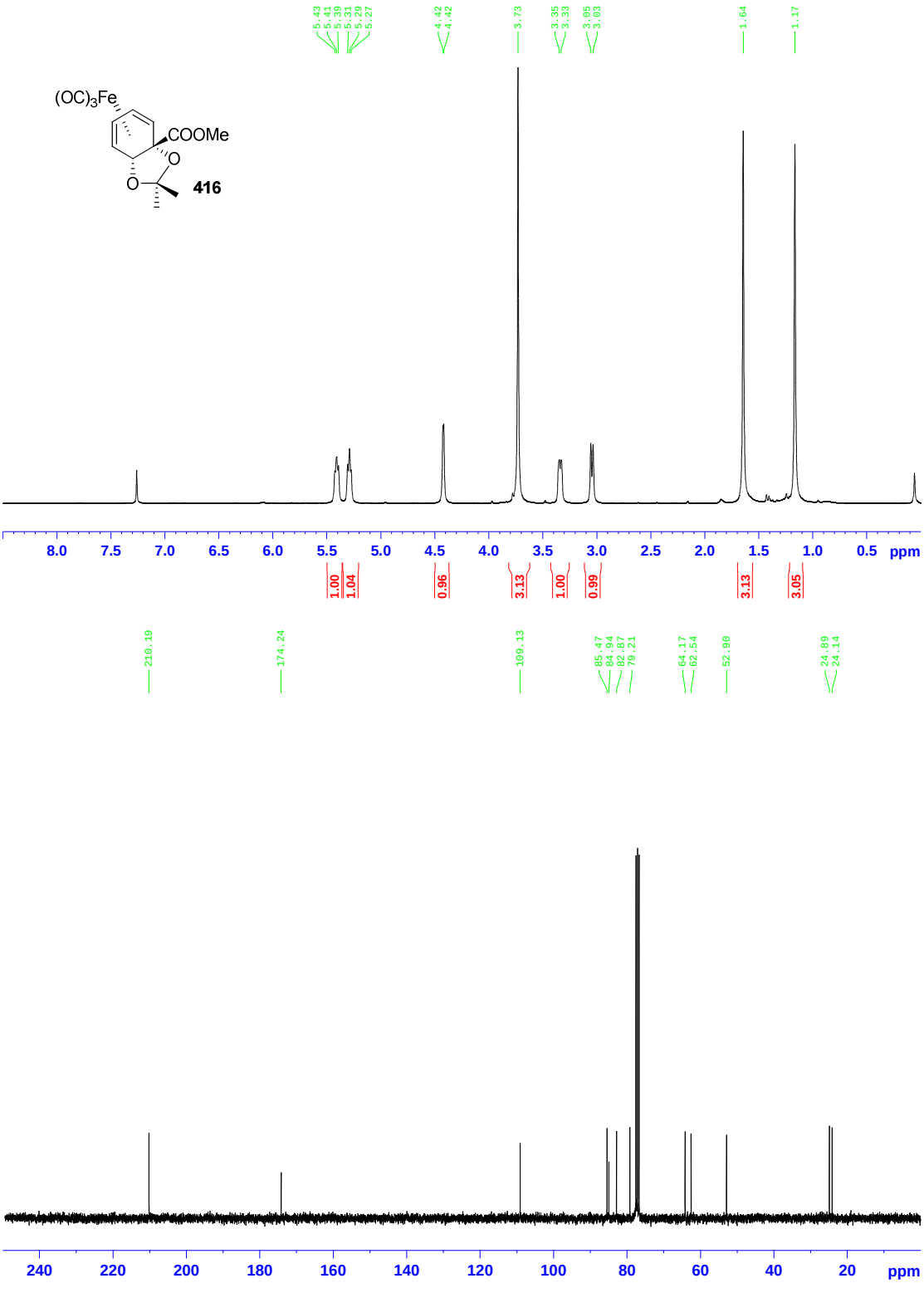
COOMe
O
O
414
5.63
5.62
5.62
5.61
5.12
5.11
3.81
3.13
3.12
3.12
3.11
3.05
3.04
3.03
3.01
1.37
1.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.04
1.00
2.99
0.98
1.03
3.31
3.09
209.40
171.51
116.97
87.16
85.83
85.74
79.96
77.58
77.16
76.74
57.60
55.81
52.88
28.13
27.19
220
200
180
160
140
120
100
80
60
40
20
ppm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COOMe
O
O
416
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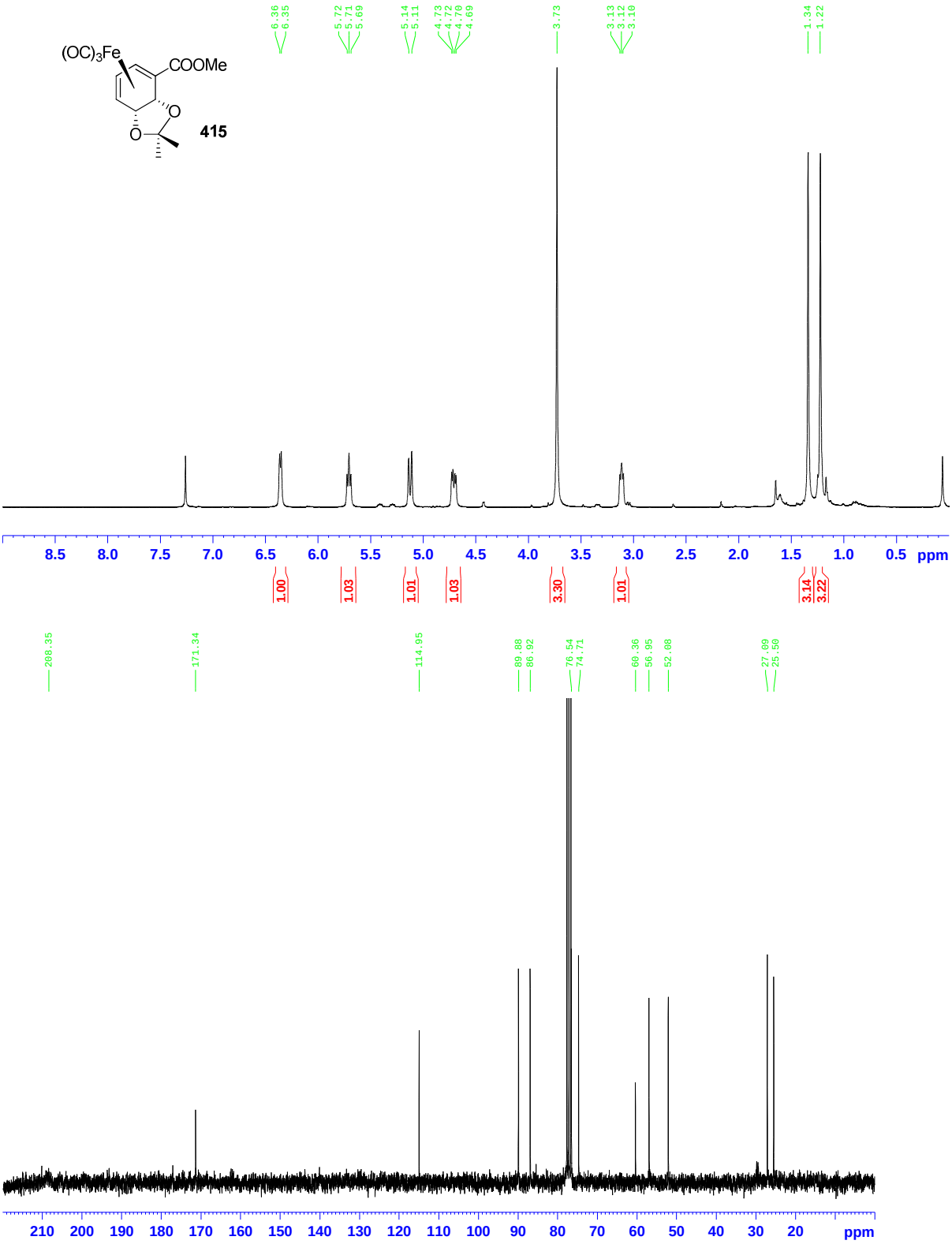
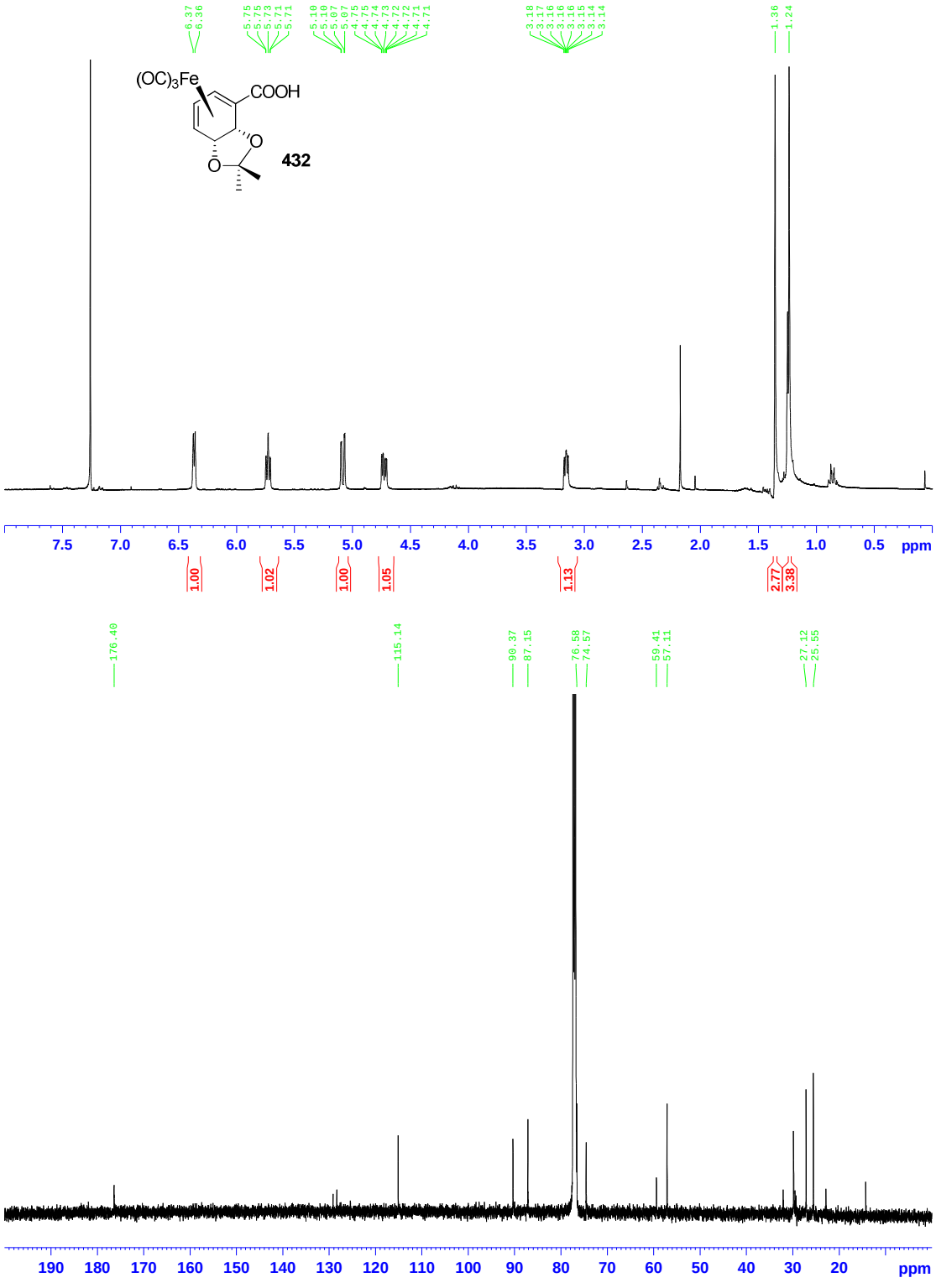
5.41
5.39
5.31
5.29
5.27
4.42
4.42
3.73
3.35
3.33
3.05
3.03
1.64
1.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
0.96
3.13
1.00
0.99
3.13
3.05
210.19
174.24
109.13
85.47
84.94
82.87
79.21
64.17
62.54
52.90
24.89
24.14
240
220
200
180
160
140
120
100
80
60
40
20
ppm


(OC)3Fe
COOMe
O
O
415
6.36
6.35
5.72
5.71
5.69
5.14
5.11
4.73
4.72
4.70
4.69
3.73
3.13
3.12
3.10
1.34
1.22
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.03
1.01
1.03
3.30
1.01
3.14
3.22
208.35
171.34
114.95
89.88
86.92
76.54
74.71
60.36
56.95
52.08
27.09
25.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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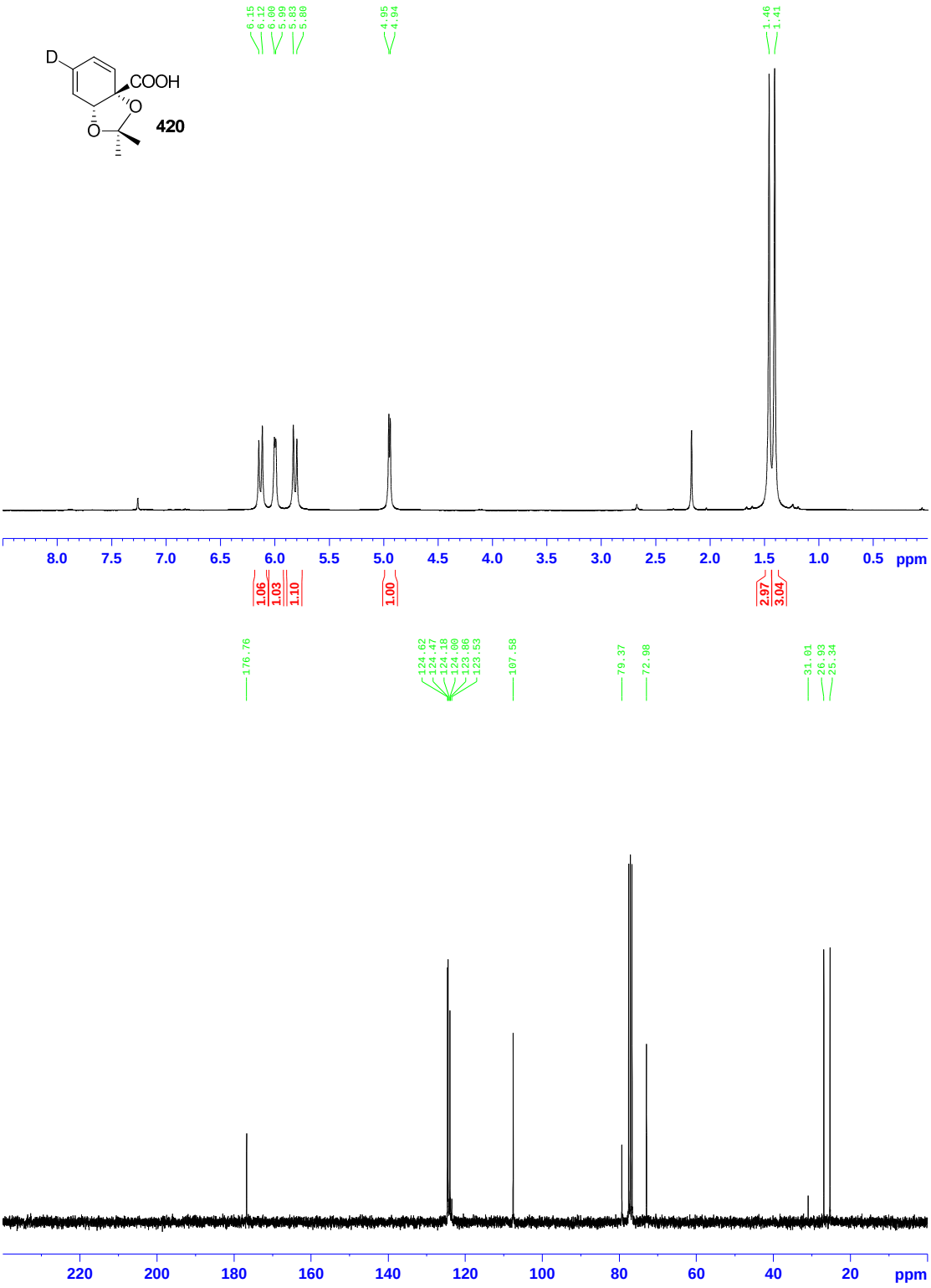
6.36
5.75
5.75
5.73
5.71
5.71
5.10
5.10
5.07
5.07
4.75
4.75
4.74
4.73
4.72
4.72
4.71
4.71
4.71
3.18
3.17
3.17
3.16
3.16
3.15
3.14
3.14
1.36
1.24
(OC)3Fe
COOH
O
O
432
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.02
1.00
1.05
1.13
2.77
3.38
176.40
115.14
90.37
87.15
76.58
74.57
59.41
57.11
27.12
25.55
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


D
COOH
O
O
420
6.15
6.12
6.00
5.99
5.83
5.80
4.95
4.94
1.46
1.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.06
1.03
1.10
1.00
2.97
3.04
176.76
124.62
124.47
124.18
124.00
123.86
123.53
107.58
79.37
72.98
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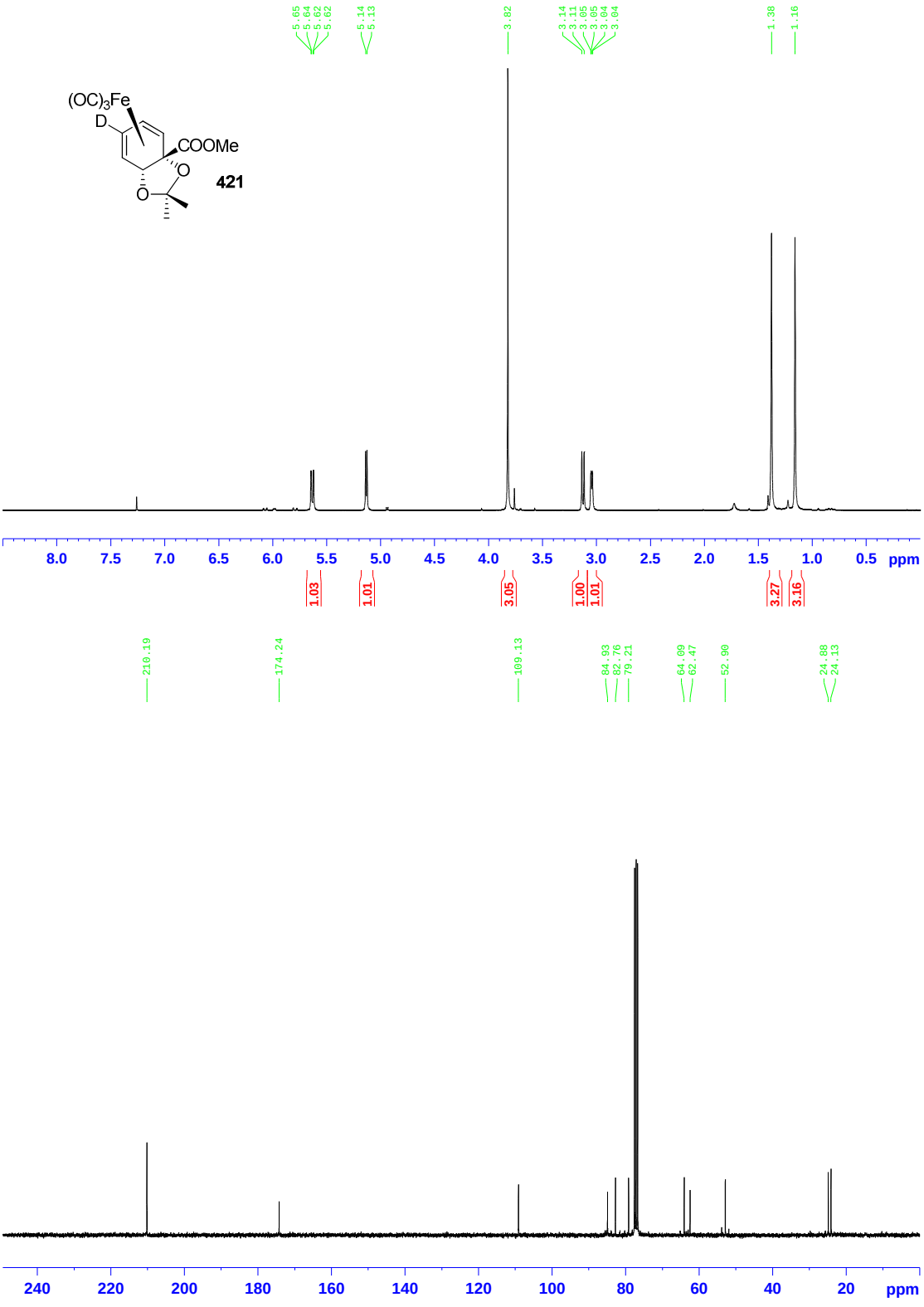
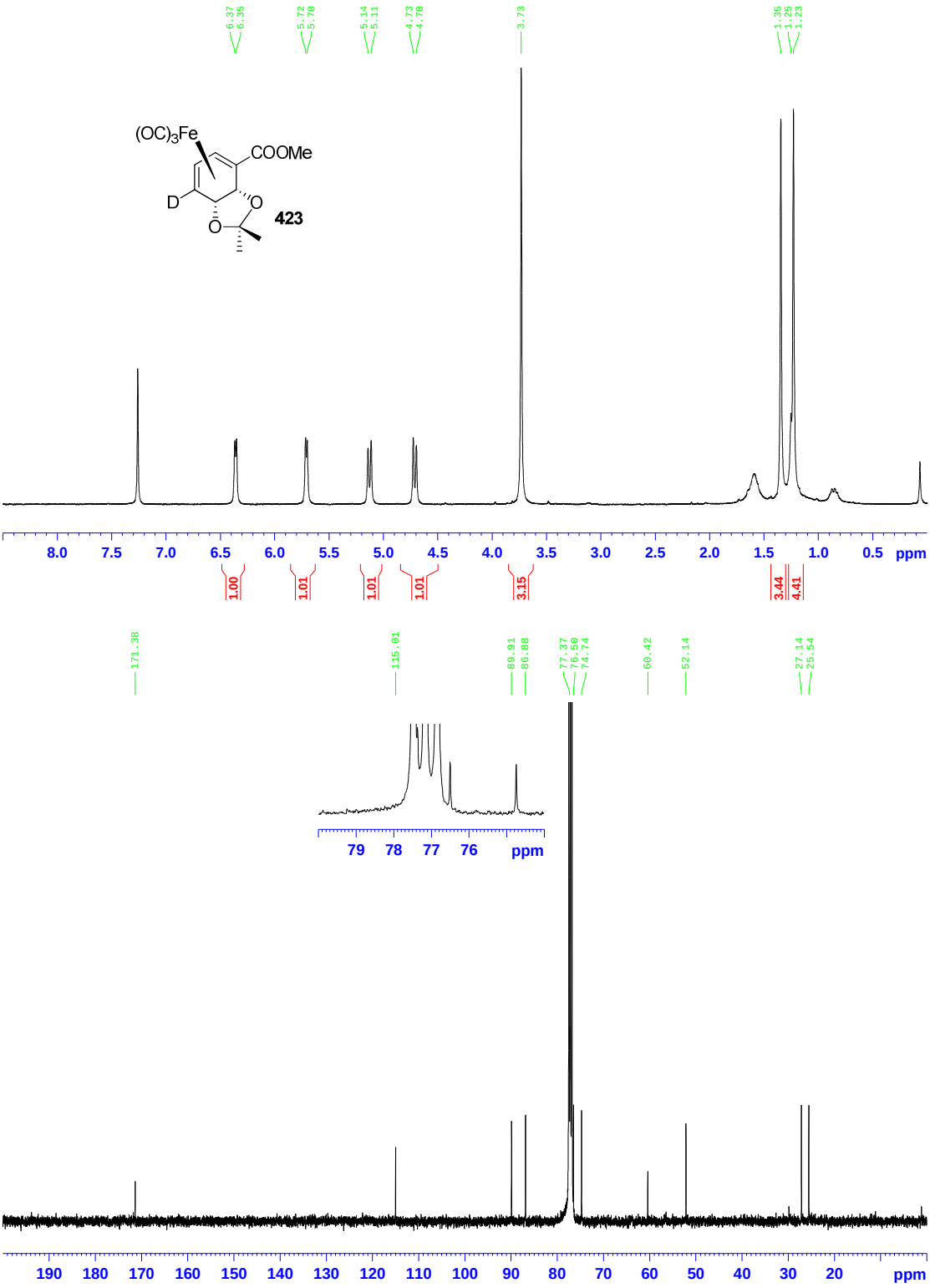
26.93
25.34
220
200
180
160
140
120
100
80
60
40
20
ppm


(OC)3Fe
D
COOMe
O
O
421
5.65
5.64
5.62
5.62
5.14
5.13
3.82
3.14
3.11
3.05
3.05
3.04
3.04
1.38
1.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
1.01
3.05
1.00
1.01
3.27
3.16
210.19
174.24
109.13
84.93
82.76
79.21
64.09
62.47
52.90
24.88
24.13
240
220
200
180
160
140
120
100
80
60
40
20
ppm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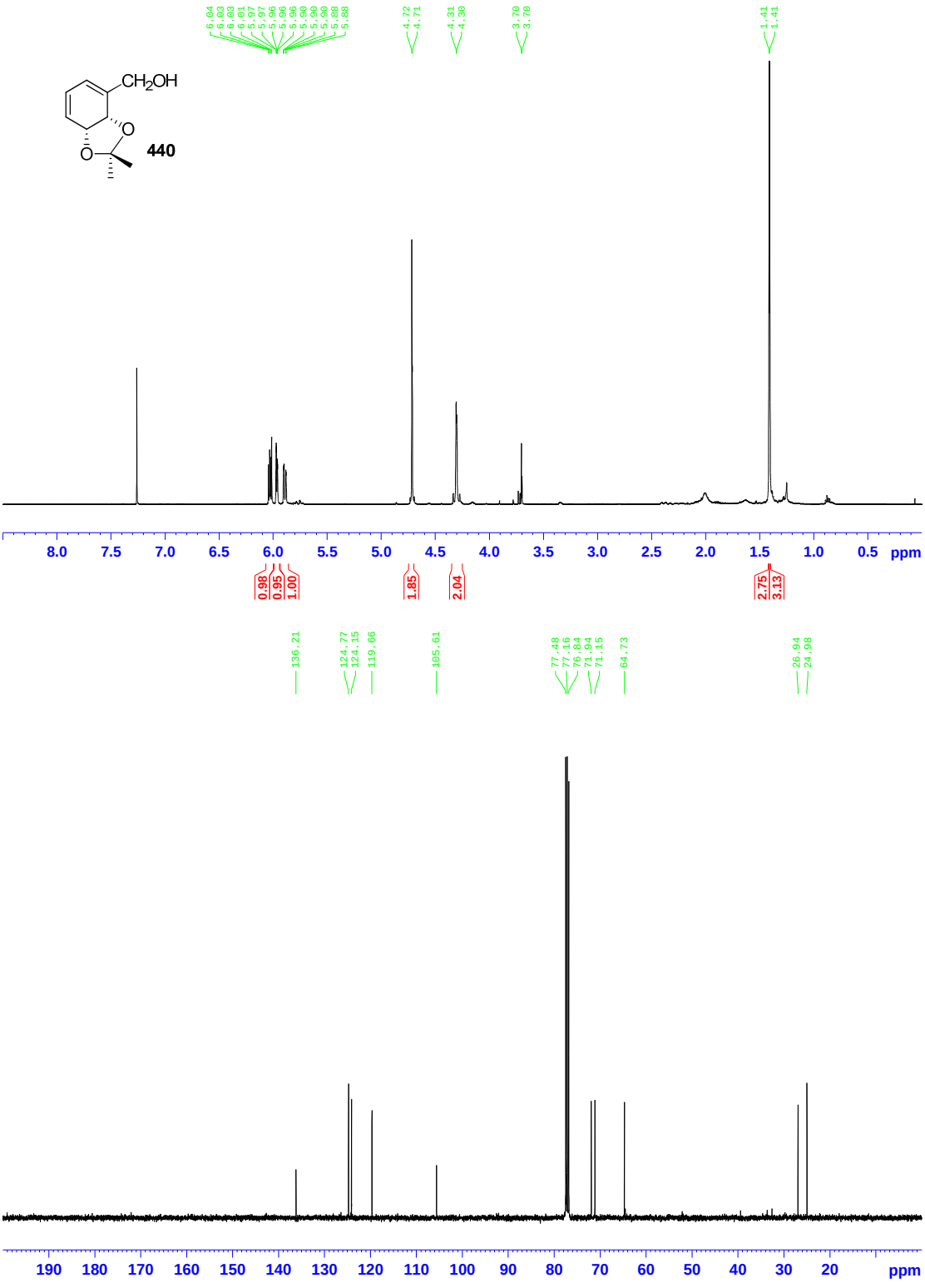
6.35
5.72
5.70
5.14
5.11
4.73
4.70
3.73
1.35
1.25
1.23
(OC)3Fe
COOMe
D
O
O
423
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
1.01
1.01
3.15
3.44
4.41
171.38
115.01
89.91
86.88
77.37
76.50
74.74
60.42
52.14
27.14
25.54
79 78 77 76 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


CH2OH
O
O
440
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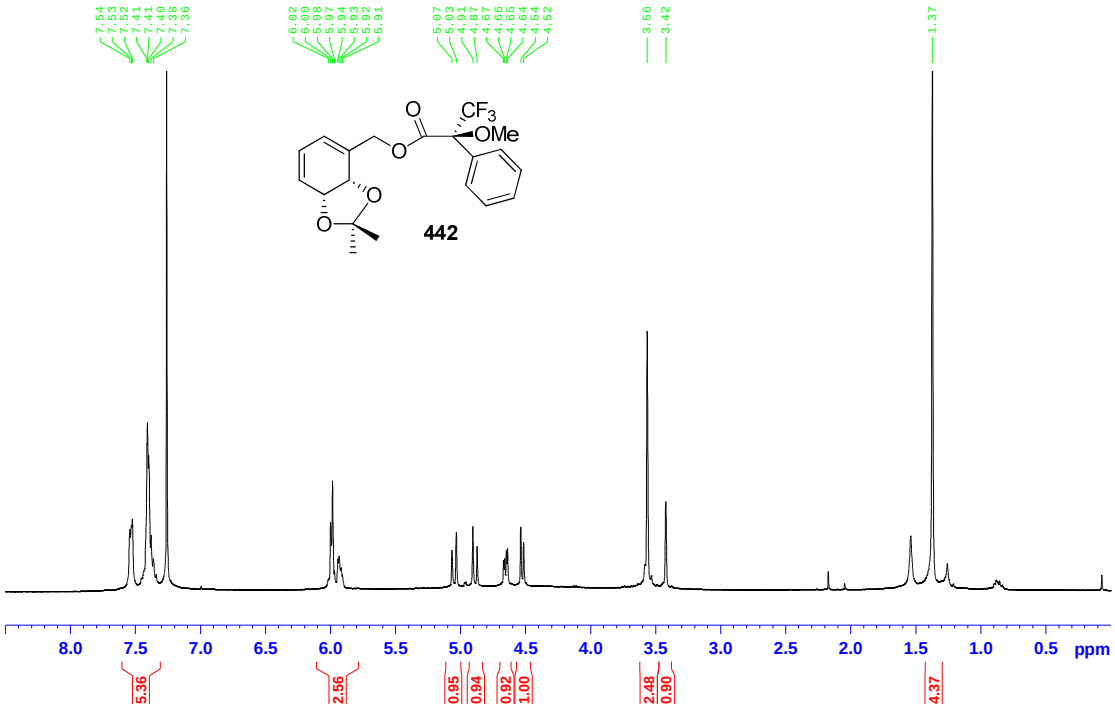
6.03
6.03
6.01
5.97
5.97
5.96
5.96
5.96
5.96
5.90
5.90
5.90
5.88
5.88
4.72
4.71
4.31
4.30
3.70
3.70
1.41
1.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.98
0.95
1.00
1.85
2.04
2.75
3.13
136.21
124.77
124.15
119.66
105.61
77.48
77.16
76.84
71.94
71.15
64.73
26.94
24.98
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.53
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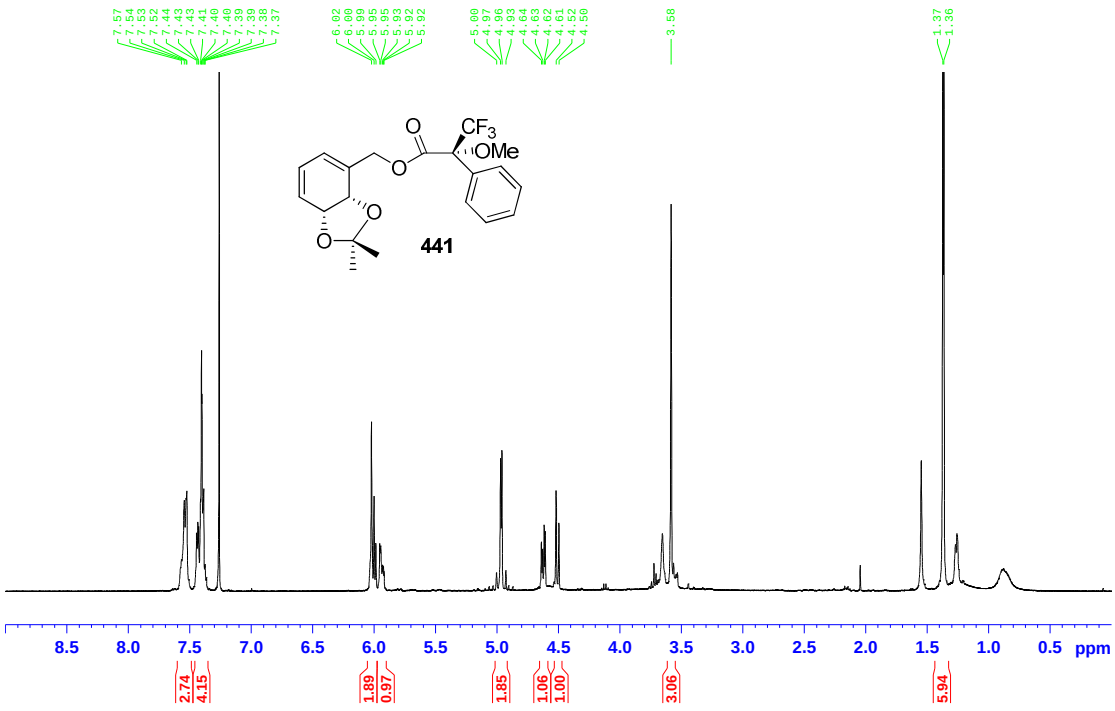
7.40
7.38
7.36
6.02
6.00
5.98
5.97
5.94
5.93
5.92
5.91
5.07
5.03
4.91
4.87
4.67
4.66
4.65
4.64
4.54
4.52
3.56
3.42
1.37
O
CF3
OMe
O
O
O
442
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.36
2.56
0.95
0.94
0.92
1.00
2.48
0.90
4.37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7.54
7.53
7.52
7.44
7.43
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.37
6.02
6.00
5.99
5.95
5.95
5.93
5.92
5.92
5.00
4.97
4.96
4.93
4.64
4.63
4.62
4.61
4.52
4.50
3.58
1.37
1.36
O
CF3
OMe
O
O
O
441
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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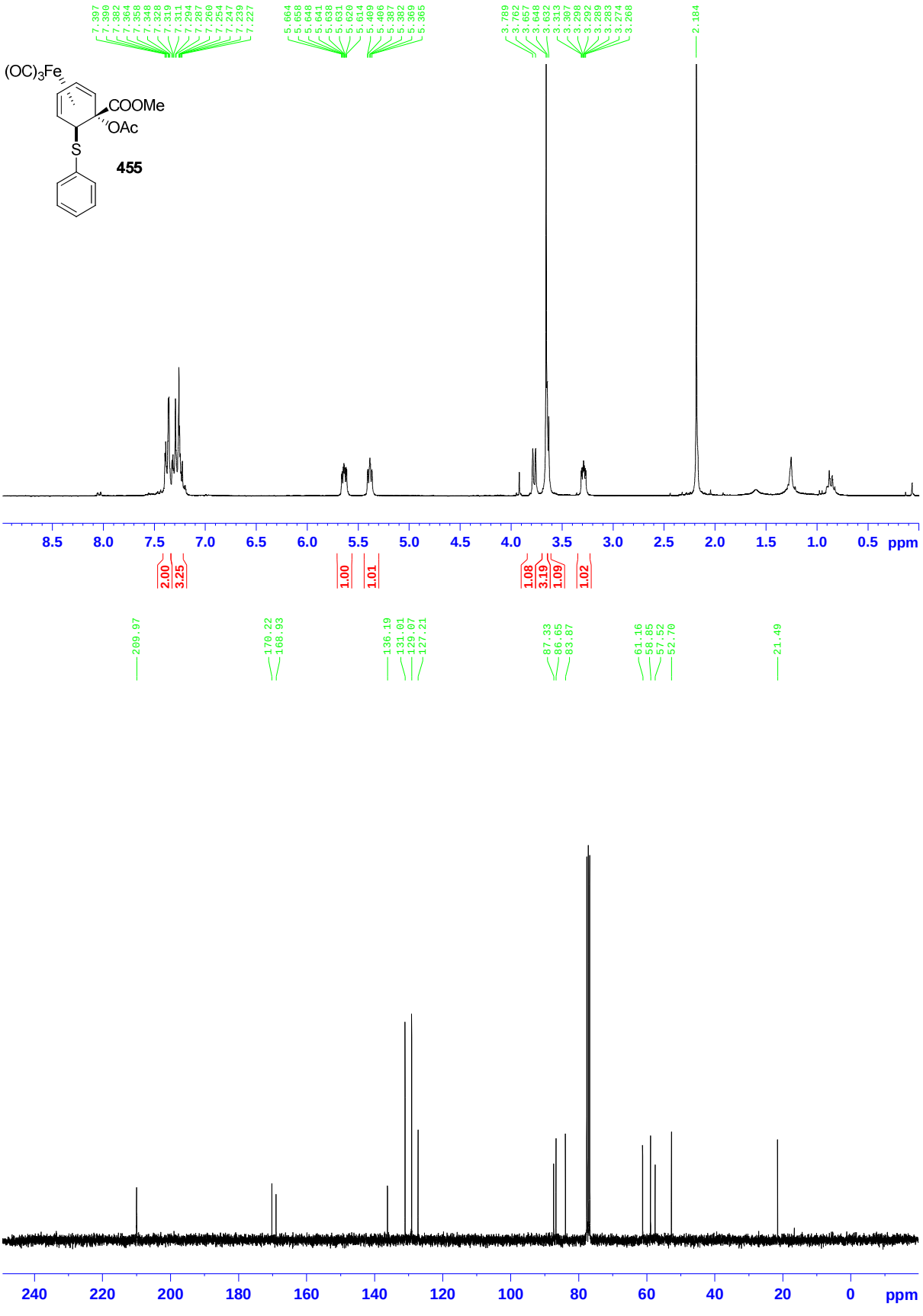
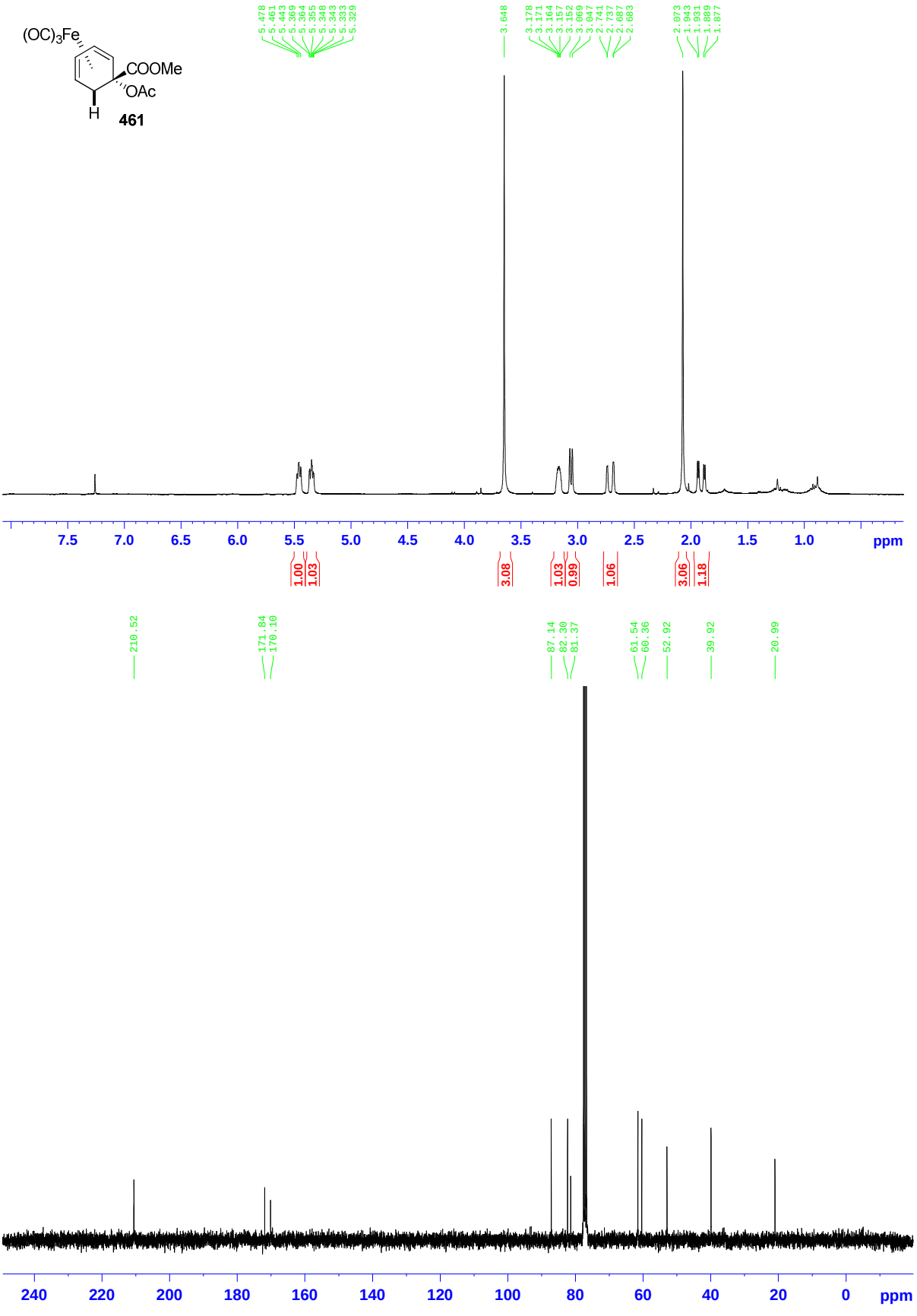
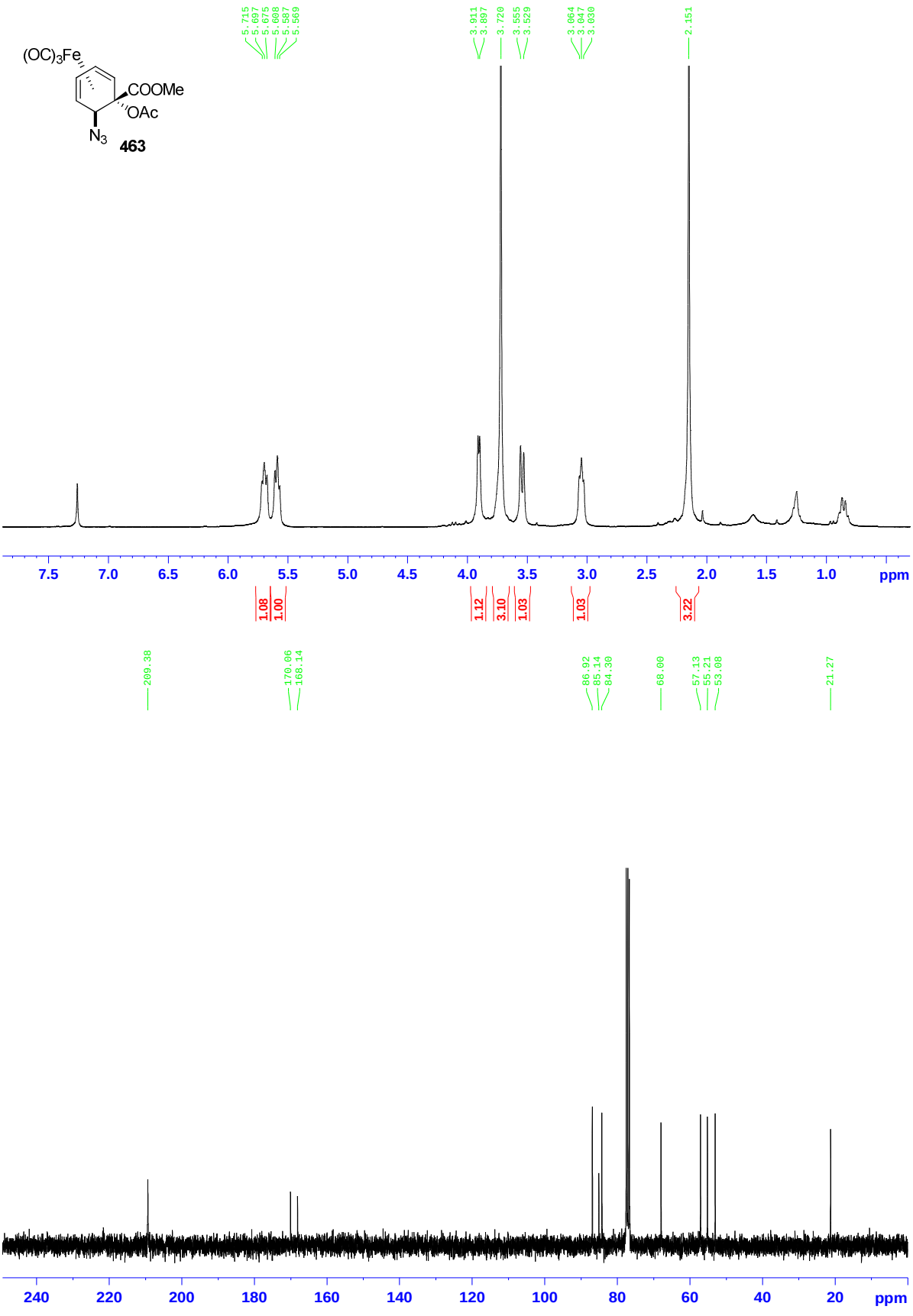
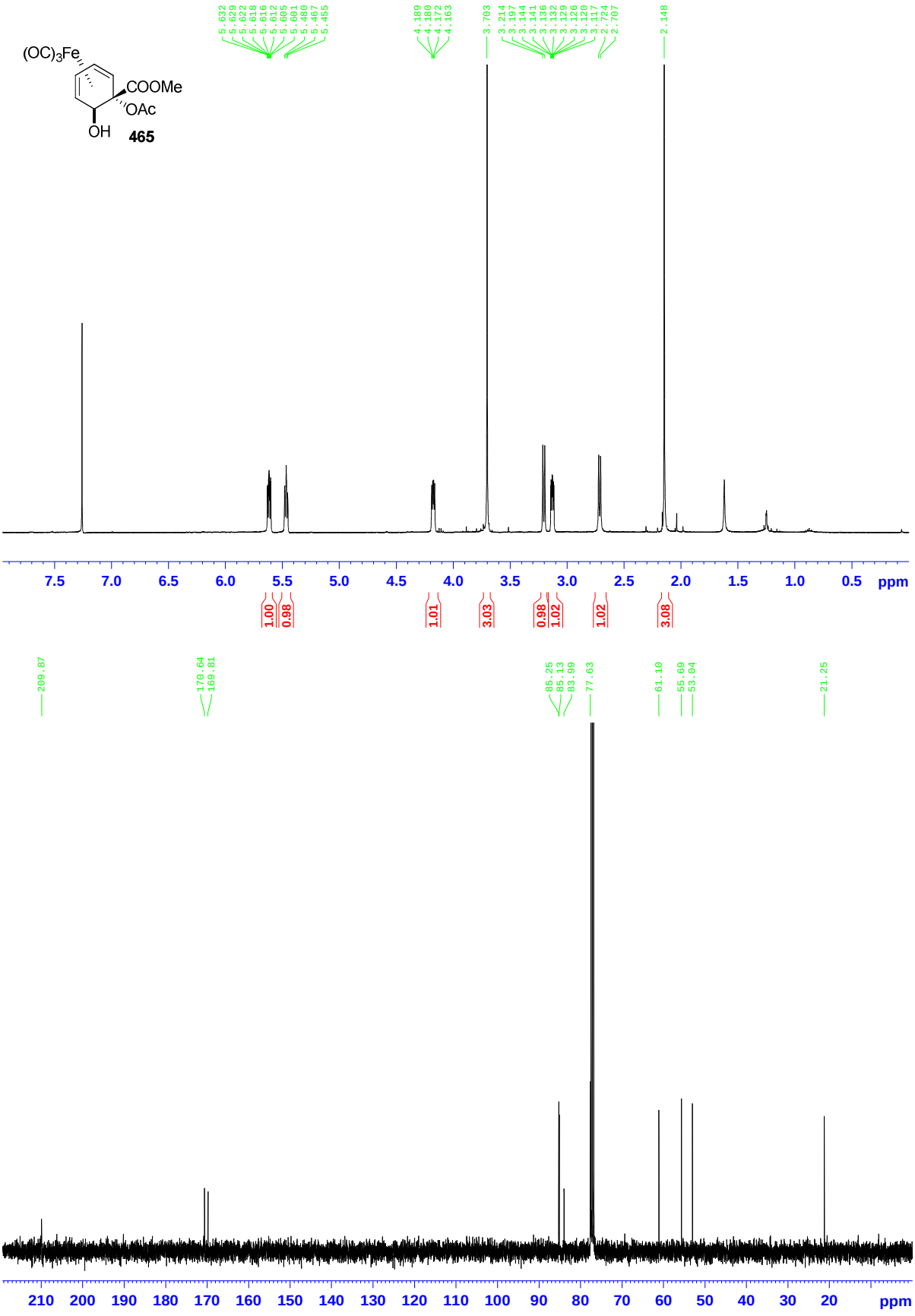
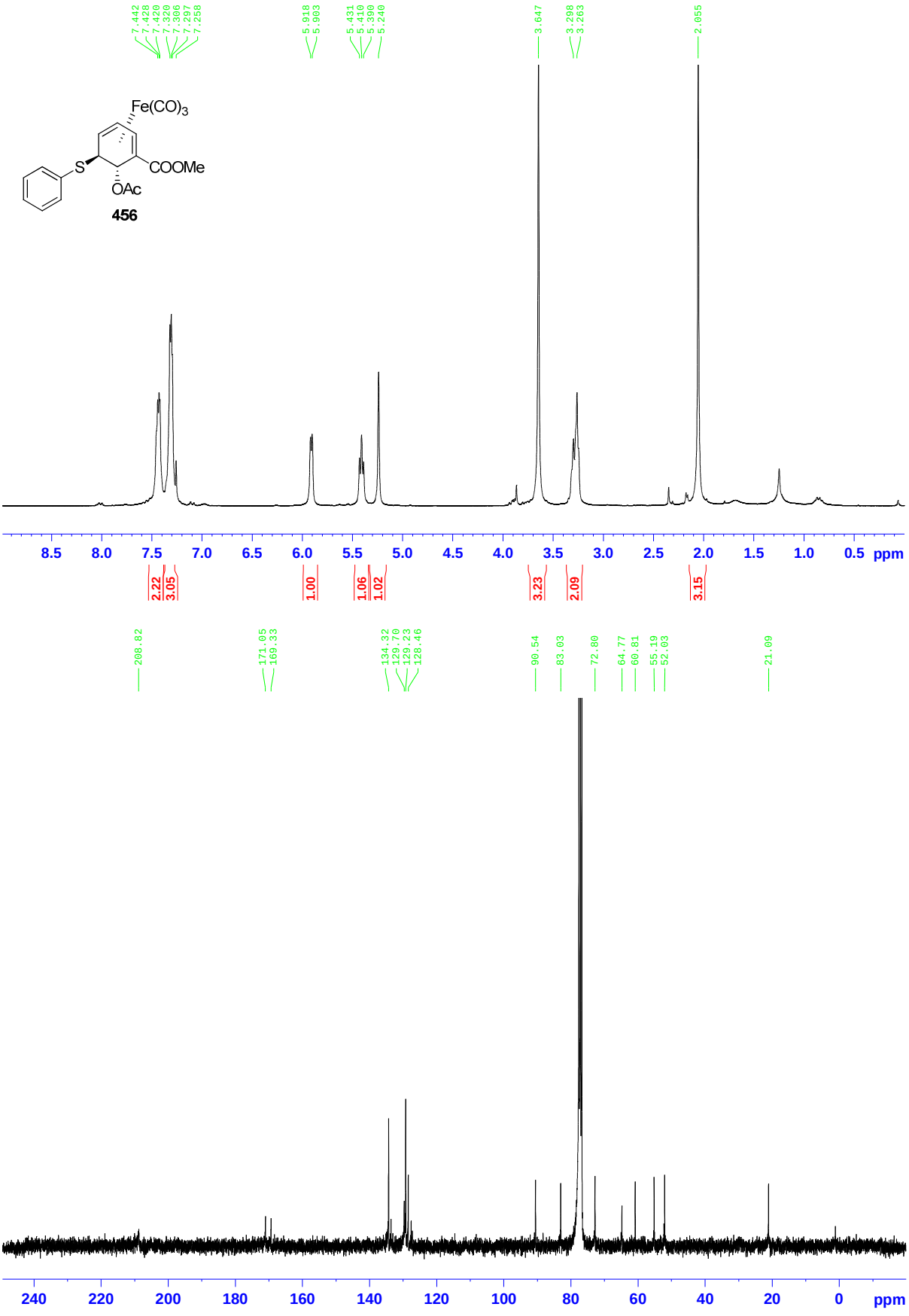
1.89
0.97
1.85
1.06
1.00
3.06
5.94

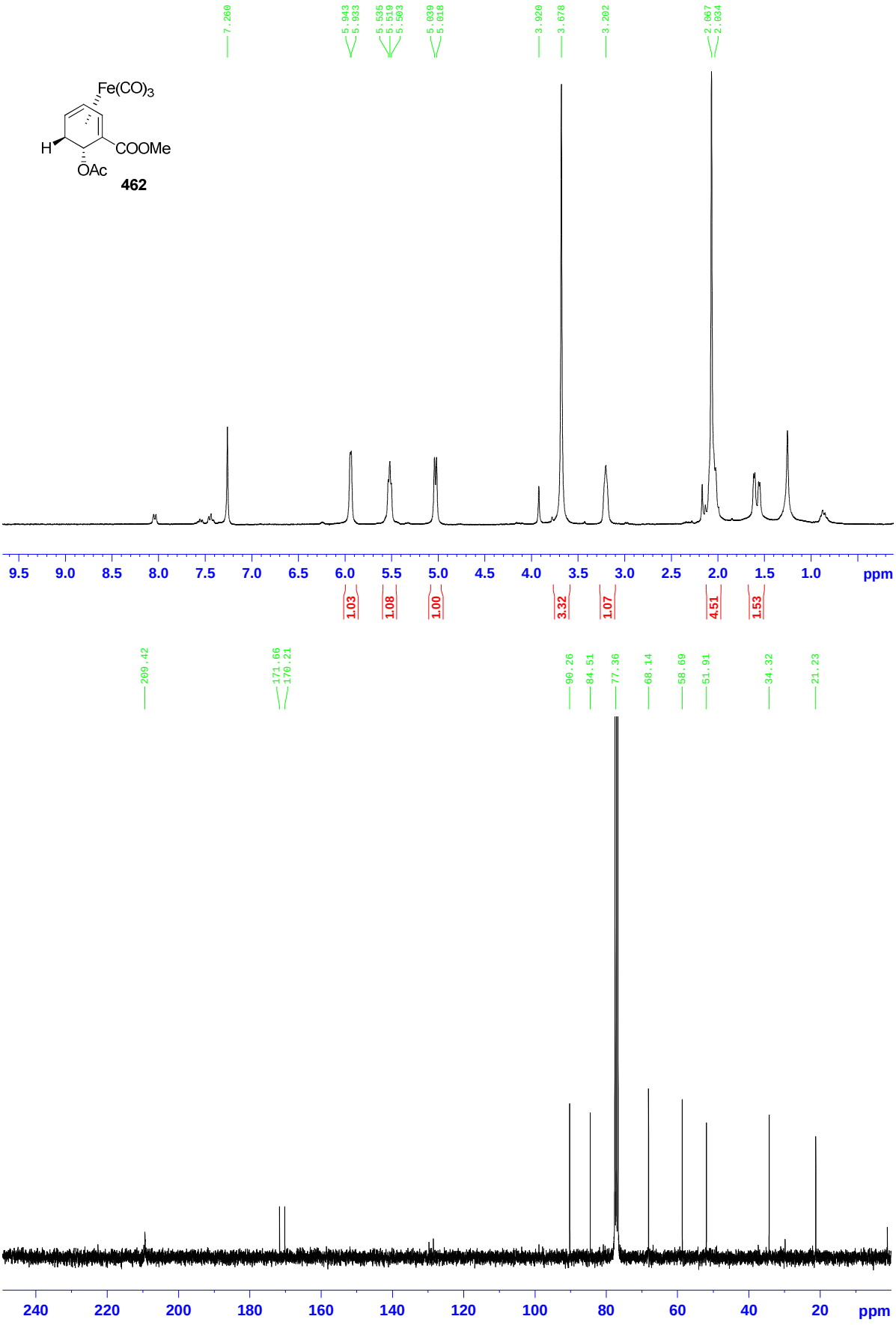

(OC)3Fe
COOMe
OAc
S
455
7.397
7.390
7.382
7.364
7.358
7.348
7.328
7.319
7.311
7.294
7.287
7.260
7.254
7.247
7.239
7.227
5.664
5.658
5.648
5.641
5.638
5.631
5.620
5.614
5.409
5.406
5.387
5.382
5.369
5.365
3.789
3.762
3.657
3.648
3.632
3.313
3.307
3.298
3.292
3.289
3.283
3.274
3.268
2.184
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
3.25
1.00
1.01
1.08
3.19
1.09
1.02
209.97
170.22
168.93
136.19
131.01
129.07
127.21
87.33
86.65
83.87
61.16
58.85
57.52
52.70
21.49
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

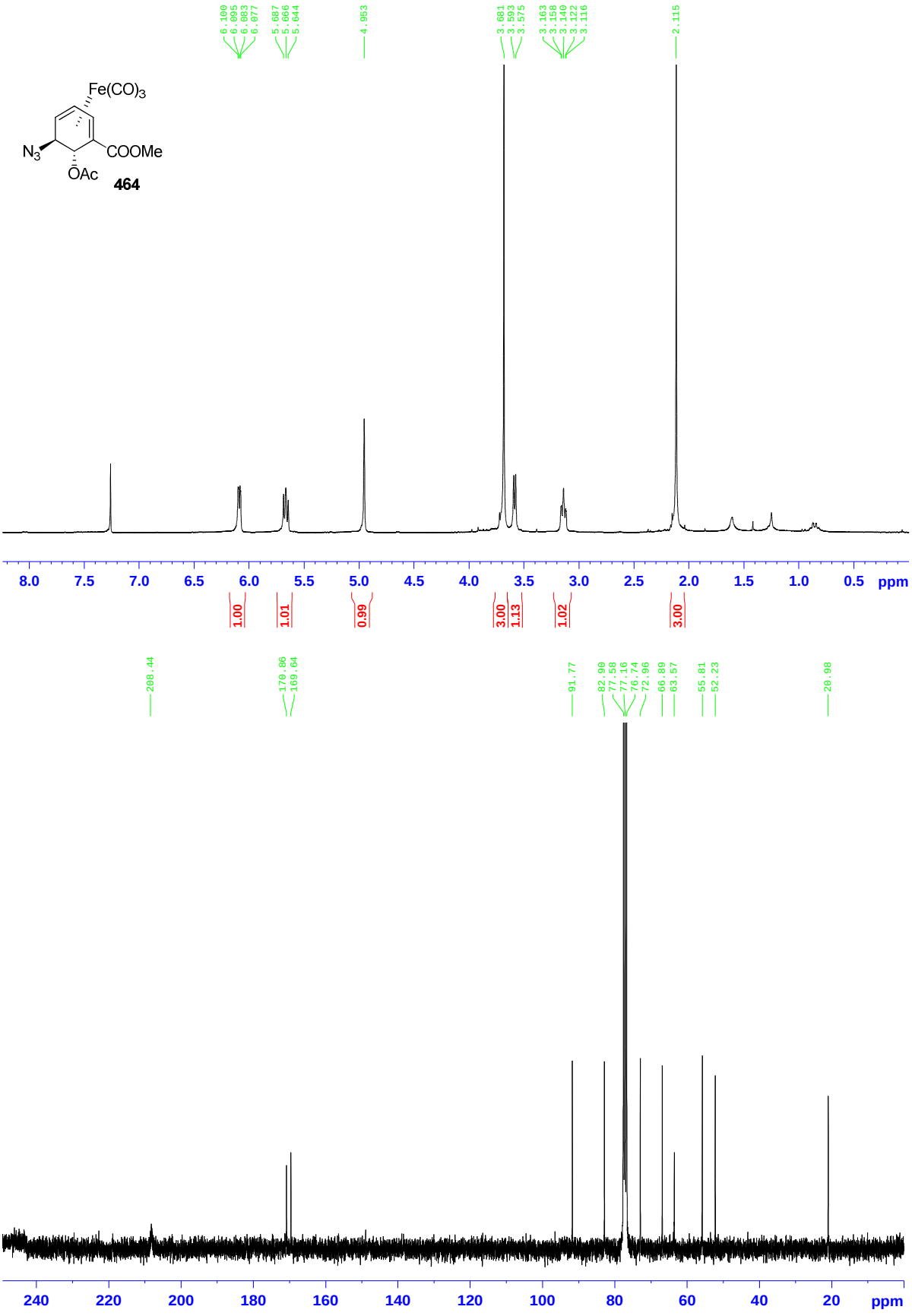

(OC)3Fe
COOMe
OAc
H
461
5.478
5.461
5.443
5.369
5.364
5.355
5.348
5.343
5.333
5.329
3.648
3.178
3.171
3.164
3.157
3.152
3.069
3.047
2.741
2.737
2.687
2.683
2.073
1.943
1.931
1.889
1.877
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.03
3.08
1.03
0.99
1.06
3.06
1.18
210.52
171.84
170.10
87.14
82.30
81.37
61.54
60.36
52.92
39.92
20.99
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

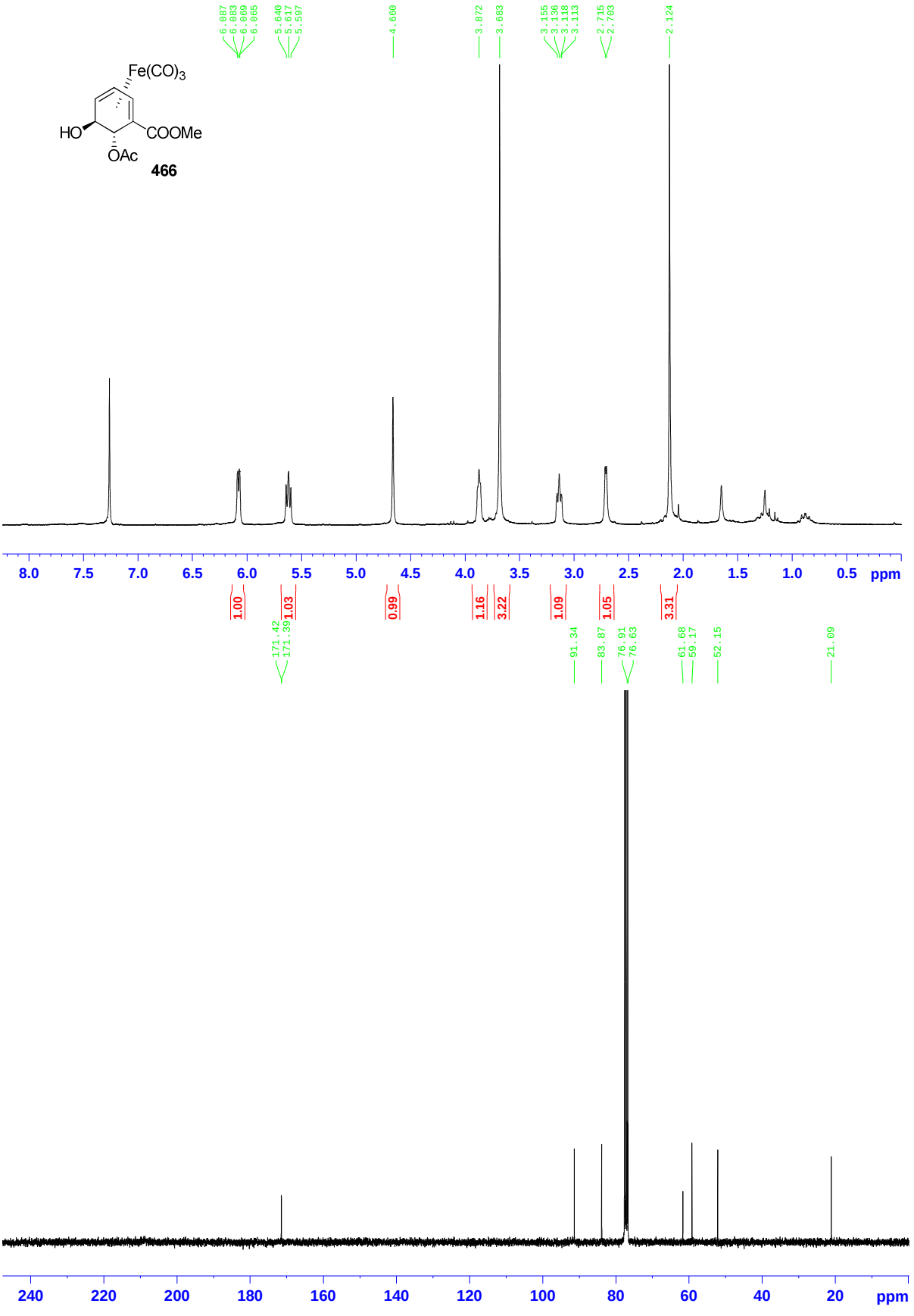

(OC)3Fe
COOMe
OAc
N3
463
5.715
5.697
5.675
5.608
5.587
5.569
3.911
3.897
3.720
3.555
3.529
3.064
3.047
3.030
2.151
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.08
1.00
1.12
3.10
1.03
1.03
3.22
209.38
170.06
168.14
86.92
85.14
84.30
68.00
57.13
55.21
53.08
21.27
240
220
200
180
160
140
120
100
80
60
40
20
ppm

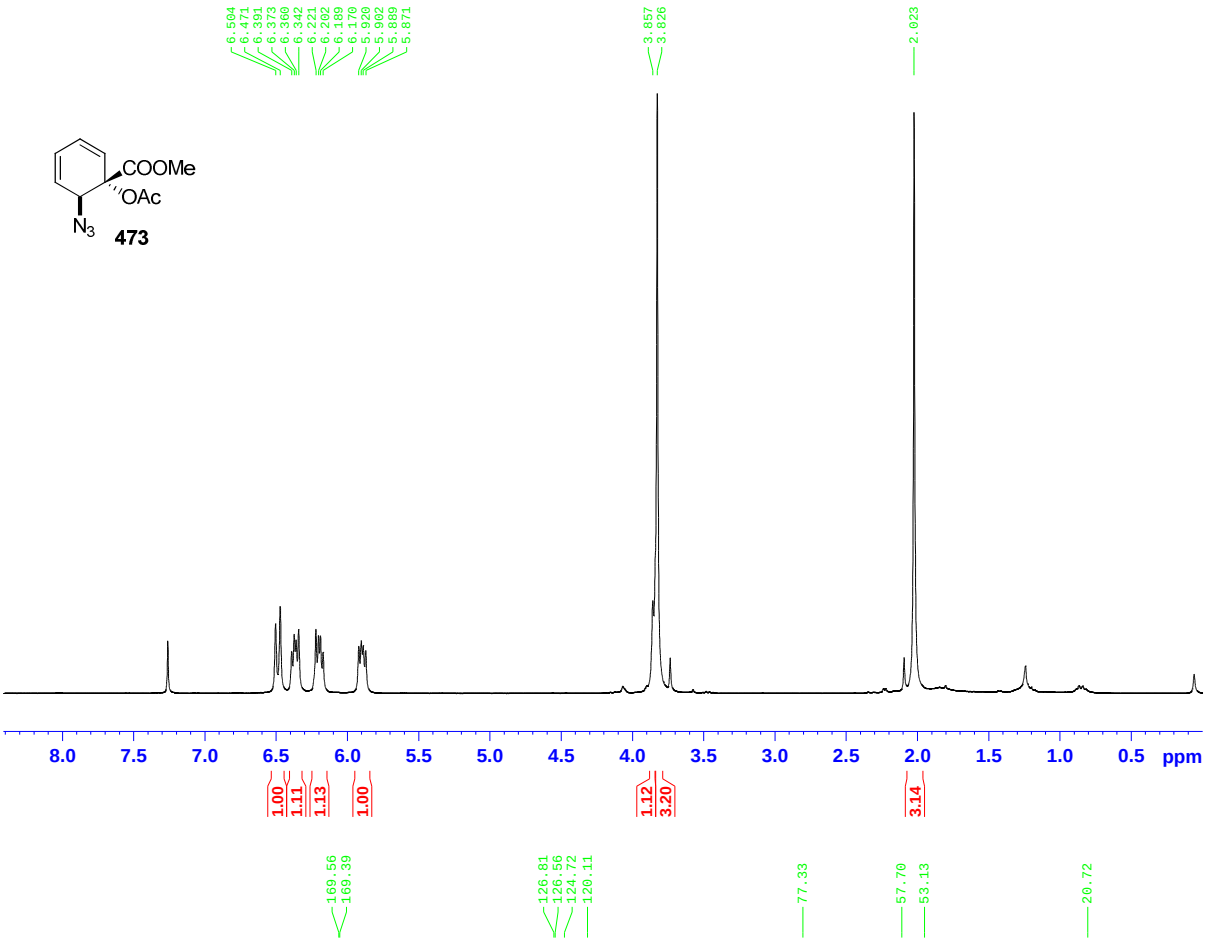

(OC)3Fe
COOMe
OAc
OH
465
5.632
5.629
5.622
5.618
5.616
5.612
5.605
5.601
5.480
5.467
5.455
4.189
4.180
4.172
4.163
3.703
3.214
3.197
3.144
3.141
3.136
3.132
3.129
3.126
3.120
3.117
2.724
2.707
2.148
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.98
1.01
3.03
0.98
1.02
1.02
3.08
209.87
170.64
169.81
85.25
85.13
83.99
77.63
61.10
55.69
53.04
21.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

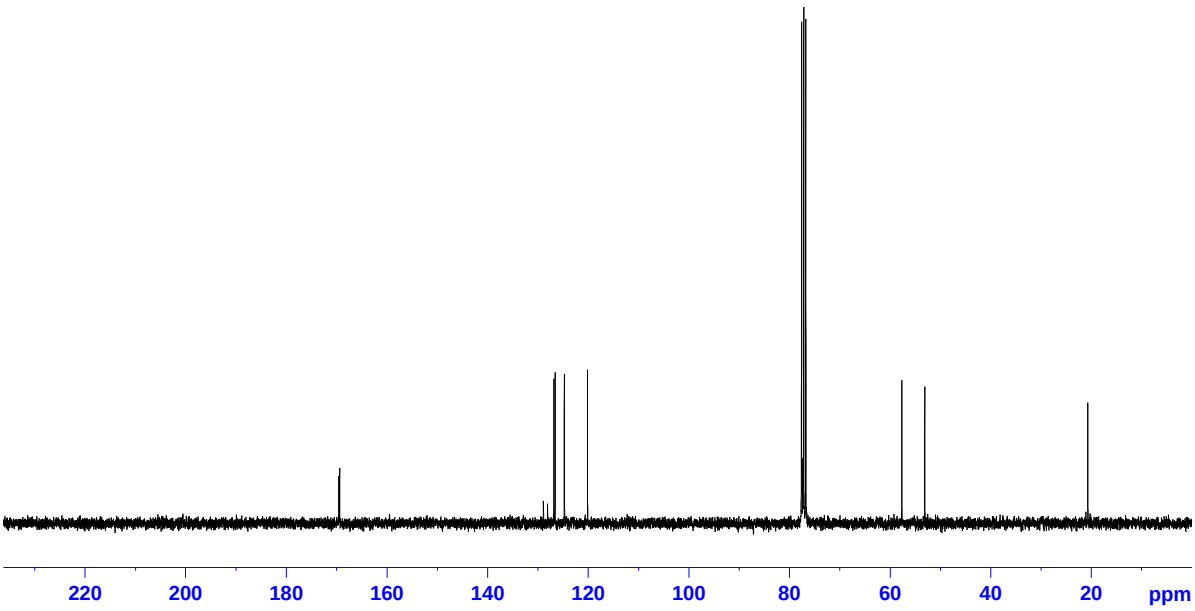

7.442
7.428
7.420
7.329
7.306
7.297
7.258
5.918
5.903
5.431
5.410
5.390
5.240
3.647
3.298
3.263
2.055
Fe(CO)3
S
COOMe
OAc
456
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.22
3.05
1.00
1.06
1.02
3.23
2.09
3.15
208.82
171.05
169.33
134.32
129.70
129.23
128.46
90.54
83.03
72.80
64.77
60.81
55.19
52.03
21.09
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

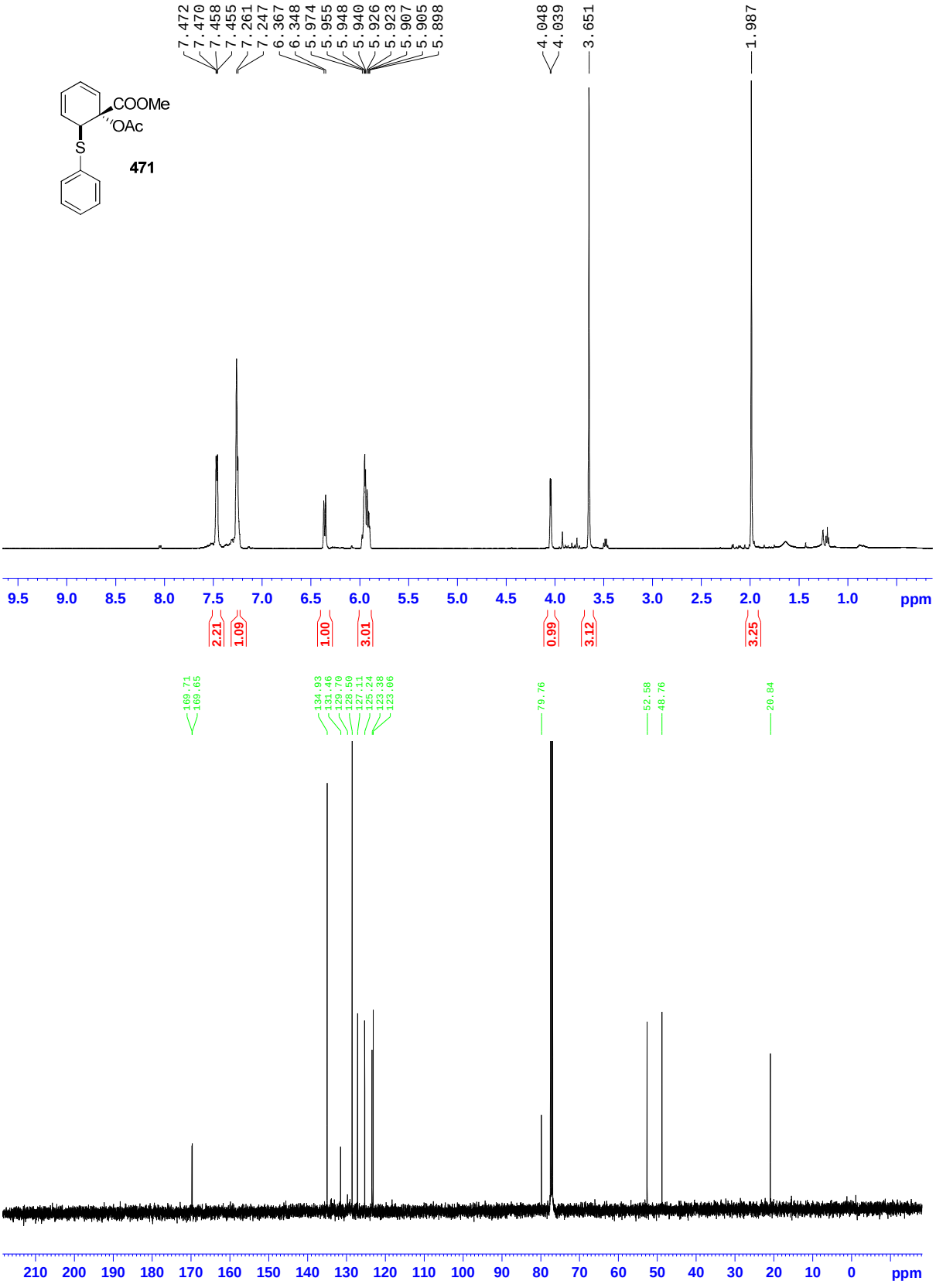

7.260
5.943
5.933
5.535
5.519
5.503
5.039
5.018
3.920
3.678
3.202
2.067
2.034
Fe(CO)3
H
COOMe
OAc
462
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.03
1.08
1.00
3.32
1.07
4.51
1.53
209.42
171.66
170.21
90.26
84.51
77.36
68.14
58.69
51.91
34.32
21.23
240 220 200 180 160 140 120 100 80 60 40 20 ppm

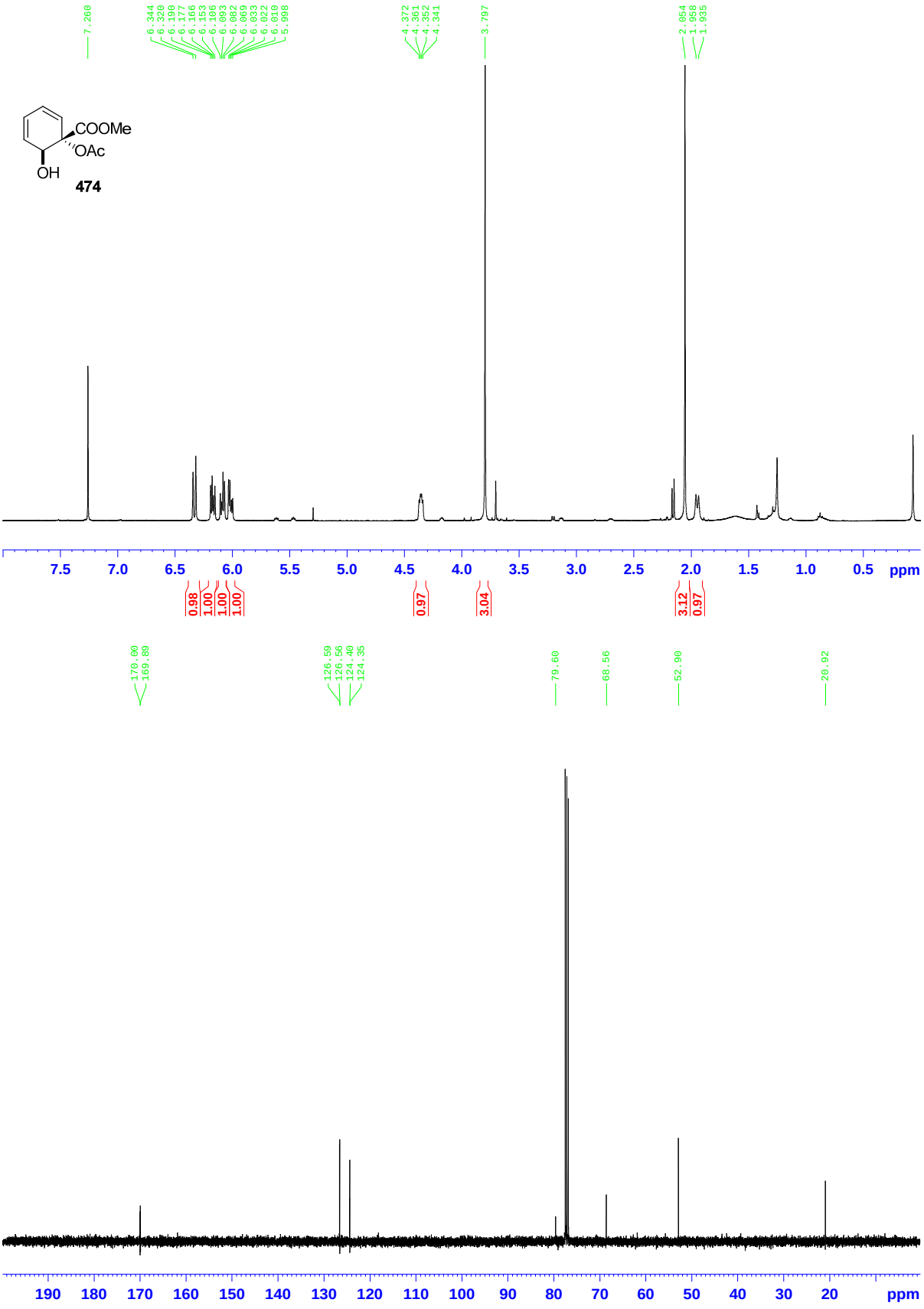

6.100
6.095
6.093
6.077
5.687
5.666
5.644
4.953
3.681
3.593
3.575
3.163
3.158
3.140
3.122
3.116
2.115
Fe(CO)3
N3
COOMe
OAc
464
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.01
0.99
3.00
1.13
1.02
3.00
208.44
170.86
169.64
91.77
82.90
77.58
77.16
76.74
72.96
66.89
63.57
55.81
52.23
20.98
240
220
200
180
160
140
120
100
80
60
40
20
ppm

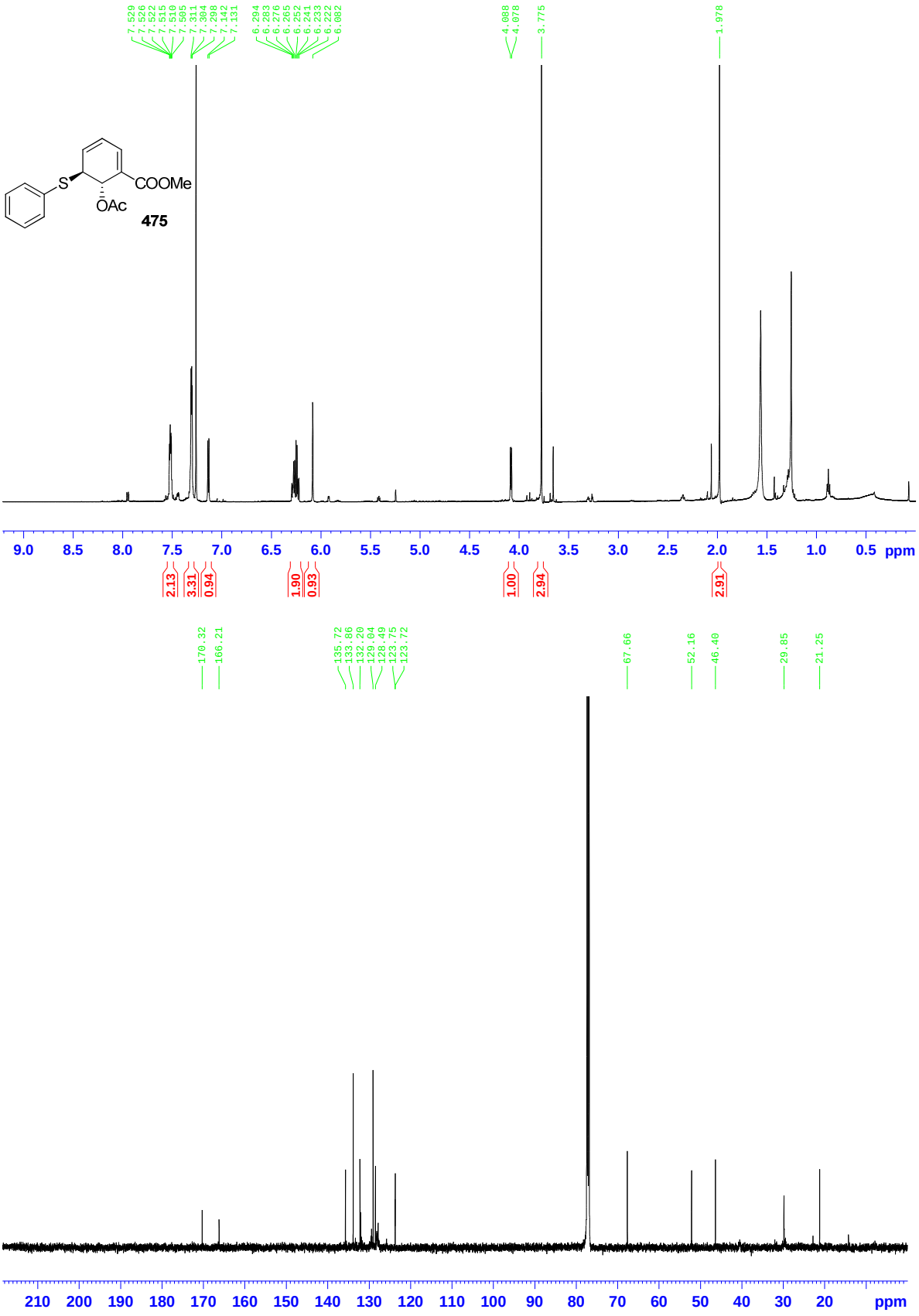

6.087
6.083
6.069
6.065
5.640
5.617
5.597
4.660
3.872
3.683
3.155
3.136
3.118
3.113
2.715
2.703
2.124
Fe(CO)3
HO
COOMe
OAc
466
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.03
0.99
1.16
3.22
1.09
1.05
3.31
171.42
171.39
91.34
83.87
76.91
76.63
61.68
59.17
52.15
21.09
240 220 200 180 160 140 120 100 80 60 40 20 ppm

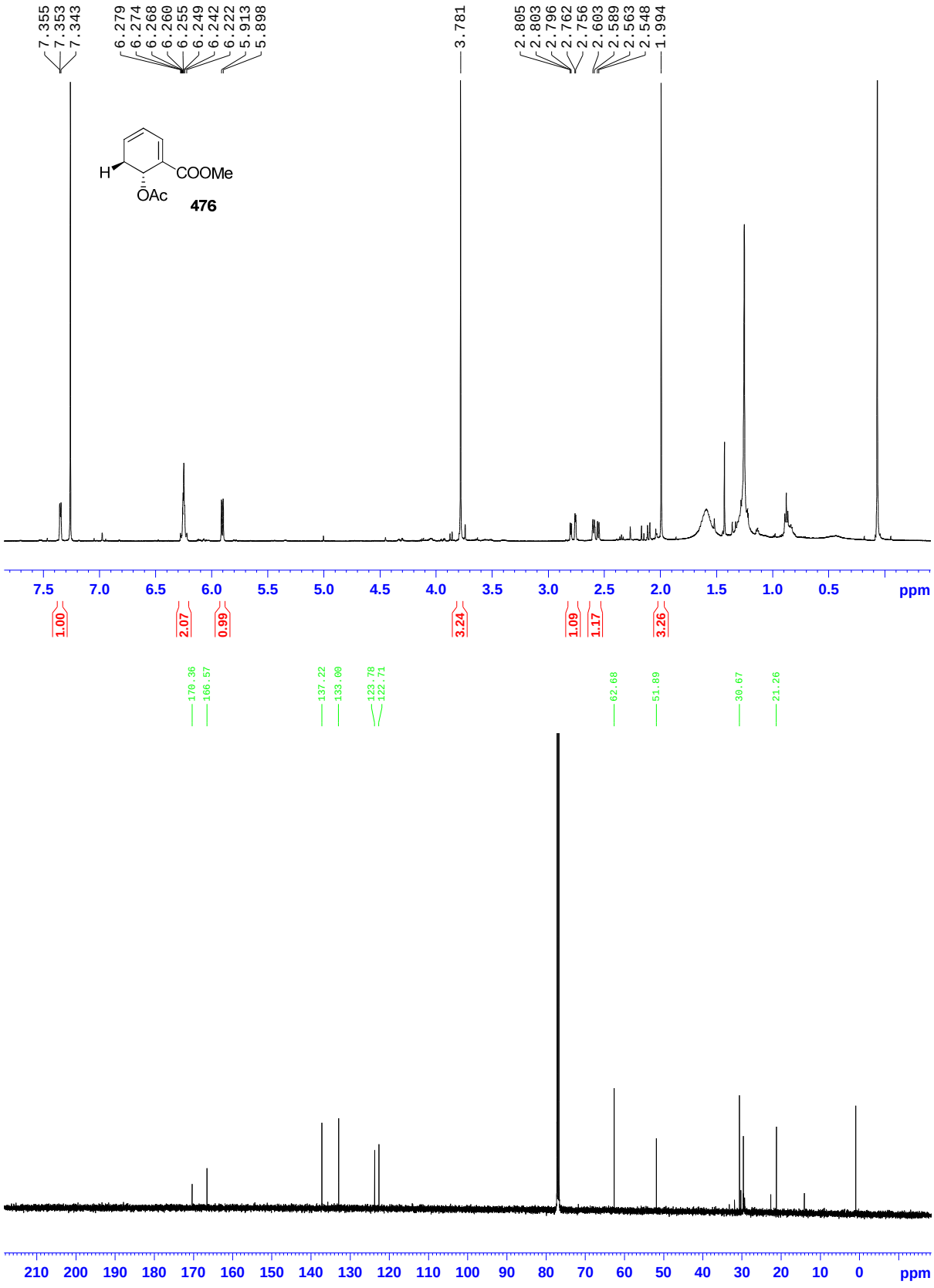

6.504
6.471
6.391
6.373
6.360
6.342
6.221
6.202
6.189
6.170
5.920
5.902
5.889
5.871
3.857
3.826
2.023
COOMe
OAc
N3
473
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.11
1.13
1.00
1.12
3.20
3.14

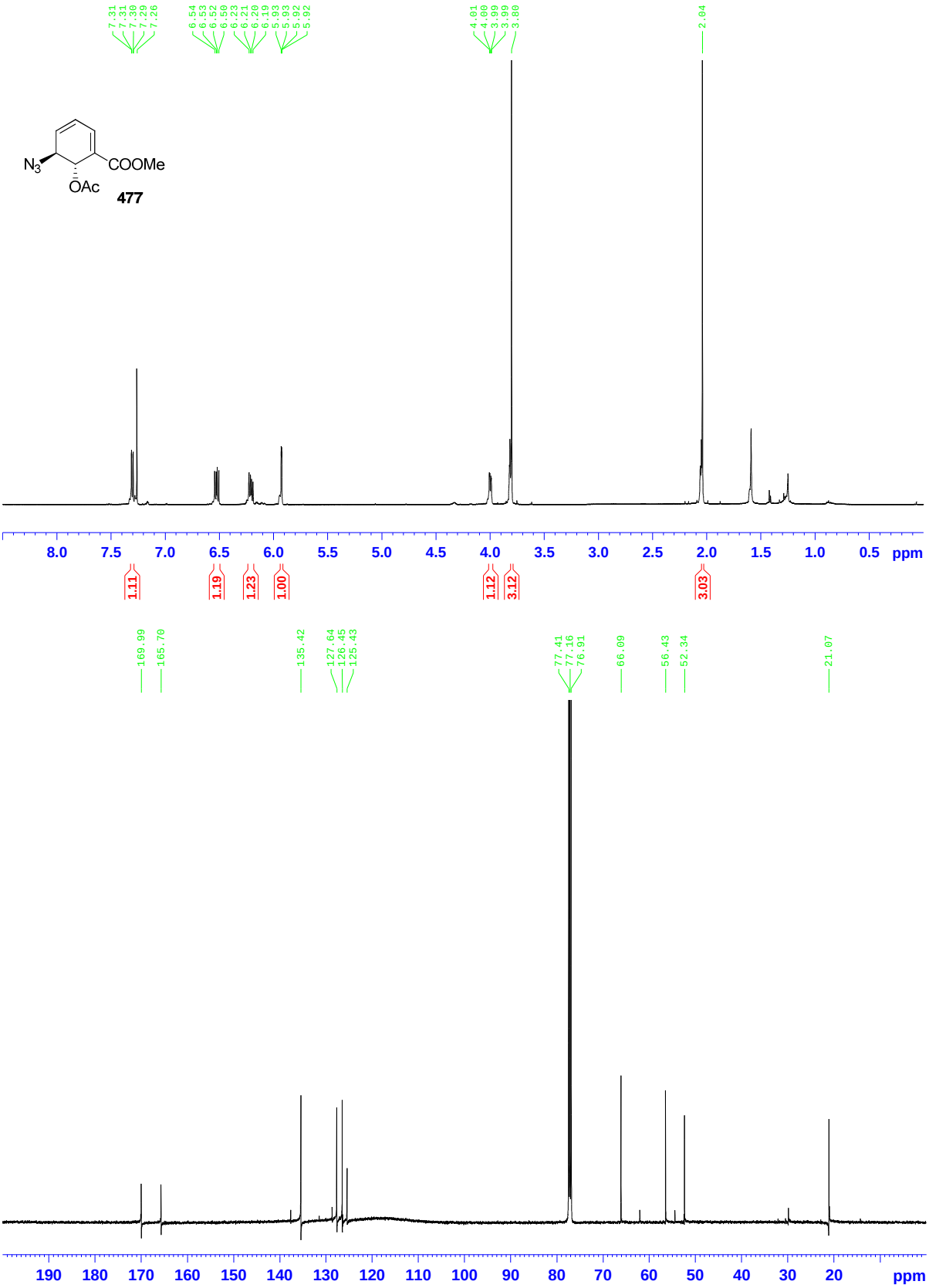

169.56
169.39
126.81
126.56
124.72
120.11
77.33
57.70
53.13
20.72
220
200
180
160
140
120
100
80
60
40
20
ppm

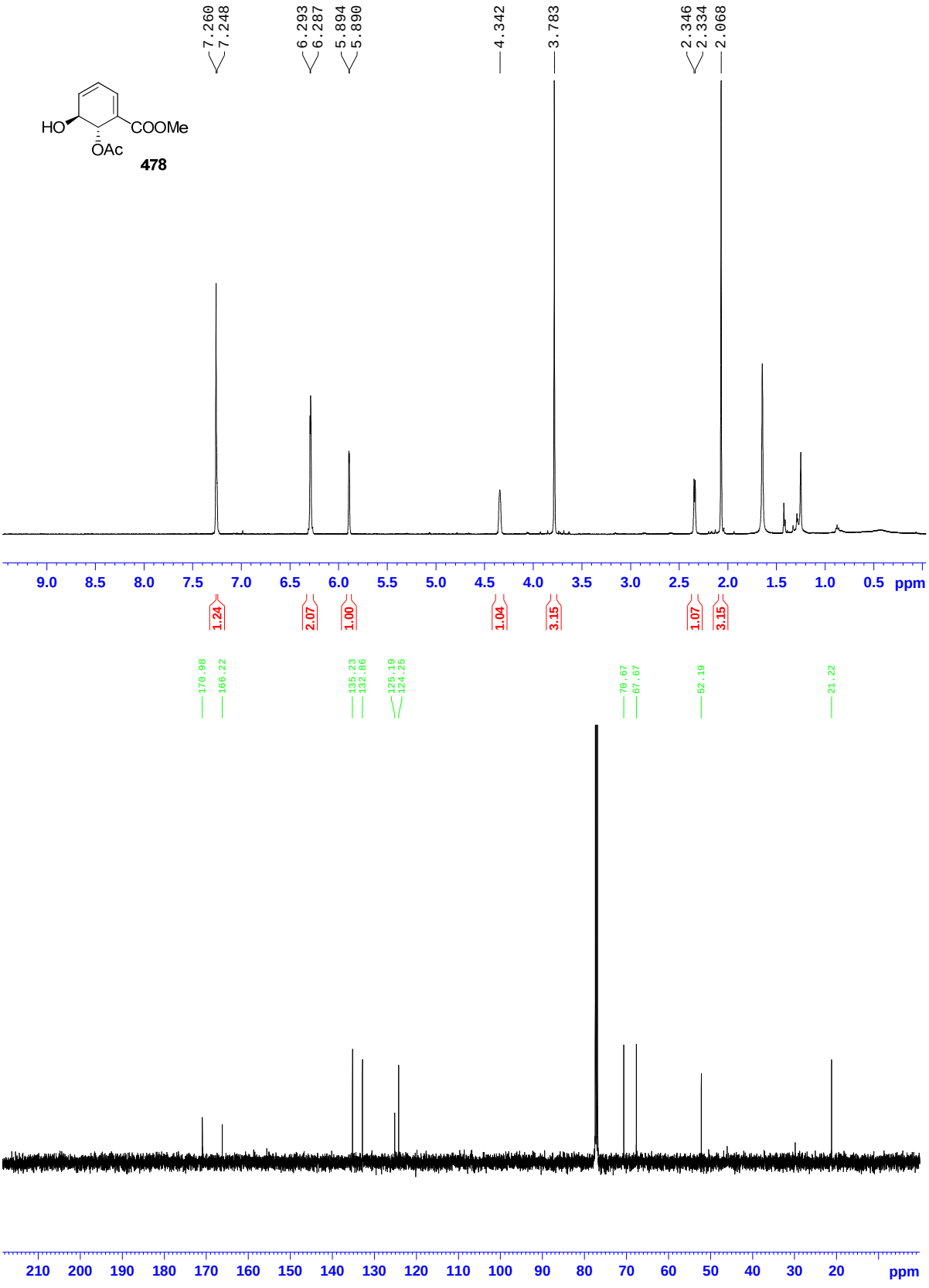

7.472
7.470
7.458
7.455
7.261
7.247
6.367
6.348
5.974
5.955
5.948
5.940
5.926
5.923
5.907
5.905
5.898
4.048
4.039
3.651
1.987
COOMe
OAc
S
471
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.21
1.09
1.00
3.01
0.99
3.12
3.25
169.71
169.65
134.93
131.46
129.70
128.50
127.11
125.24
123.38
123.06
79.76
52.58
48.76
20.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
6.344
6.320
6.190
6.177
6.166
6.153
6.106
6.093
6.082
6.069
6.033
6.022
6.010
5.998
4.372
4.361
4.352
4.341
3.797
2.054
1.958
1.935
COOMe
OAc
OH
474
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
1.00
1.00
1.00
0.97
3.04
3.12
0.97
170.00
169.89
126.59
126.56
124.40
124.35
79.60
68.56
52.90
20.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.529
7.526
7.522
7.515
7.506
7.505
7.311
7.304
7.298
7.142
7.131
6.294
6.283
6.276
6.265
6.252
6.241
6.233
6.222
6.082
4.088
4.078
3.775
1.978
S
COOMe
OAc
475
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.13
3.31
0.94
1.90
0.93
1.00
2.94
2.91
170.32
166.21
135.72
133.86
132.20
129.04
128.49
123.75
123.72
67.66
52.16
46.40
29.85
21.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.355
7.353
7.343
6.279
6.274
6.268
6.260
6.255
6.249
6.242
6.222
5.913
5.898
3.781
2.805
2.803
2.796
2.762
2.756
2.603
2.589
2.563
2.548
1.994
H
COOMe
OAc
476
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.07
0.99
3.24
1.09
1.17
3.26
170.36
166.57
137.22
133.00
123.78
122.71
62.68
51.89
30.67
21.26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.31
7.31
7.30
7.29
7.26
6.54
6.53
6.52
6.50
6.23
6.21
6.20
6.19
5.93
5.93
5.92
5.92
4.01
4.00
3.99
3.99
3.80
2.04
N3
COOMe
OAc
477
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.11
1.19
1.23
1.00
1.12
3.12
3.03
169.99
165.70
135.42
127.64
126.45
125.43
77.41
77.16
76.91
66.09
56.43
52.34
21.07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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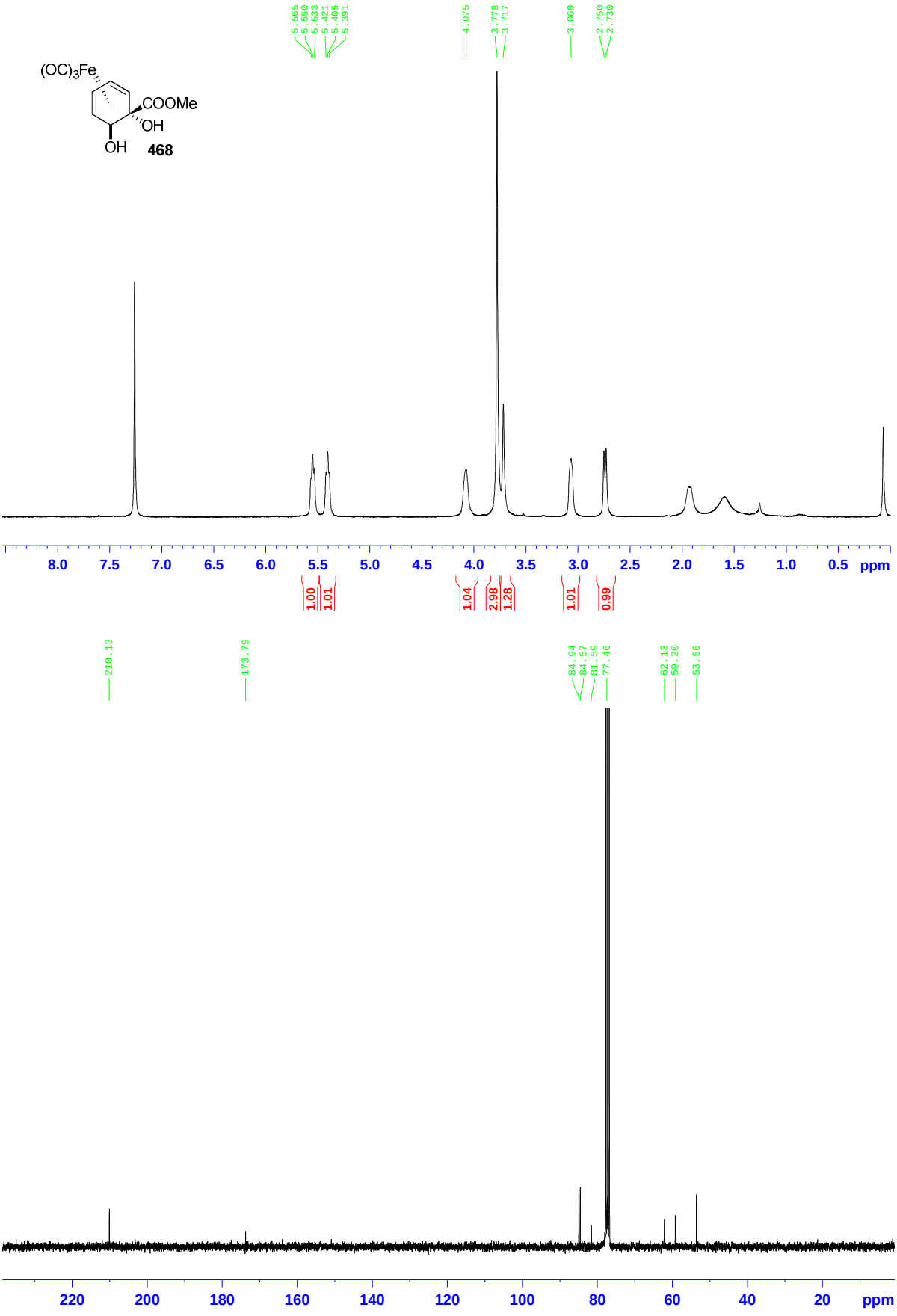
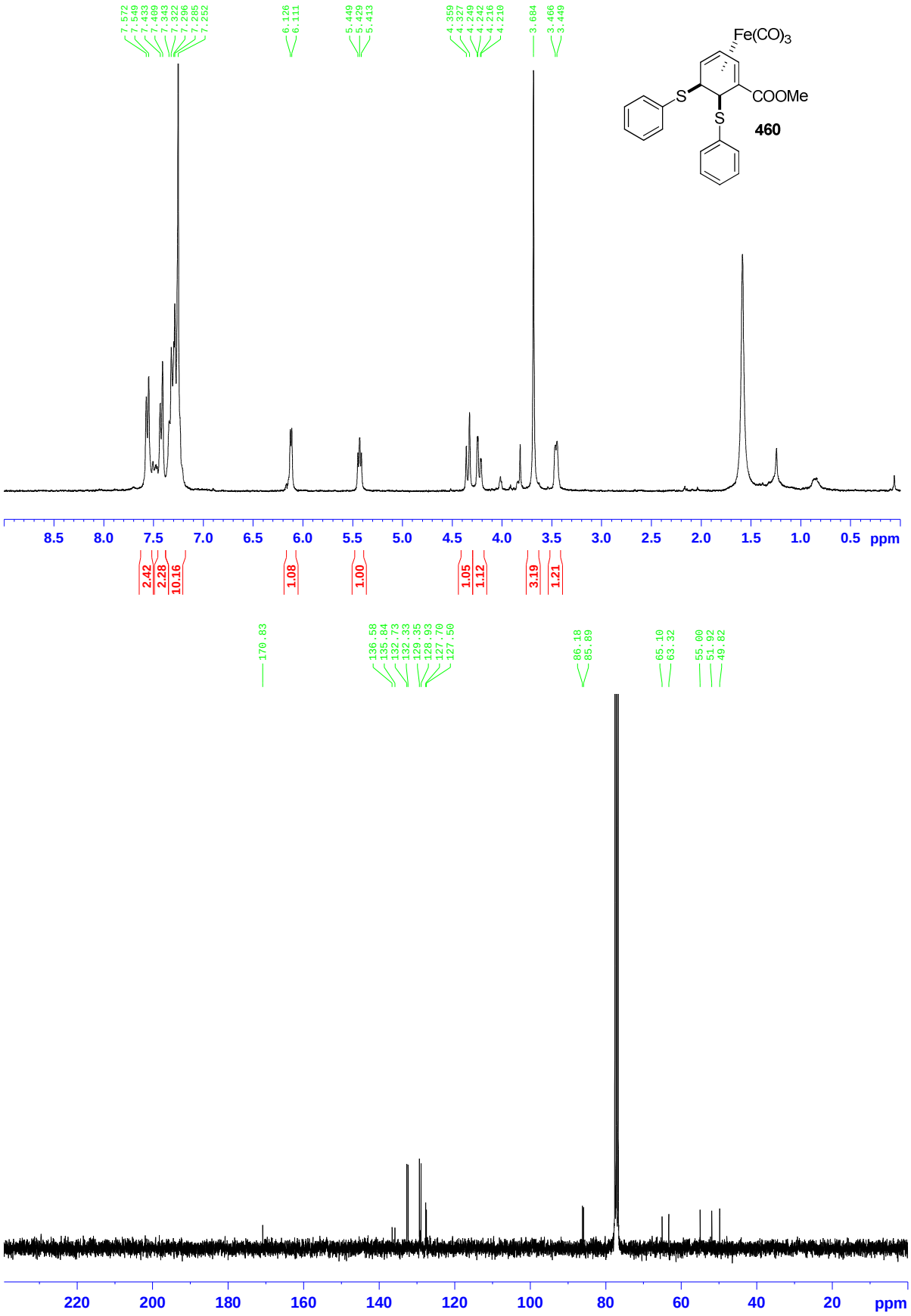
7.248
6.293
6.287
5.894
5.890
4.342
3.783
2.346
2.334
2.068
HO
COOMe
OAc
478
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.24
2.07
1.00
1.04
3.15
1.07
3.15
170.98
166.22
135.23
132.86
125.19
124.25
70.67
67.67
52.19
21.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


(OC)3Fe
COOMe
OH
OH
468
5.565
5.550
5.533
5.421
5.405
5.391
4.075
3.778
3.717
3.069
2.750
2.730
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.01
1.04
2.98
1.28
1.01
0.99
210.13
173.79
84.94
84.57
81.59
77.46
62.13
59.20
53.56
220 200 180 160 140 120 100 80 60 40 20 ppm


7.572
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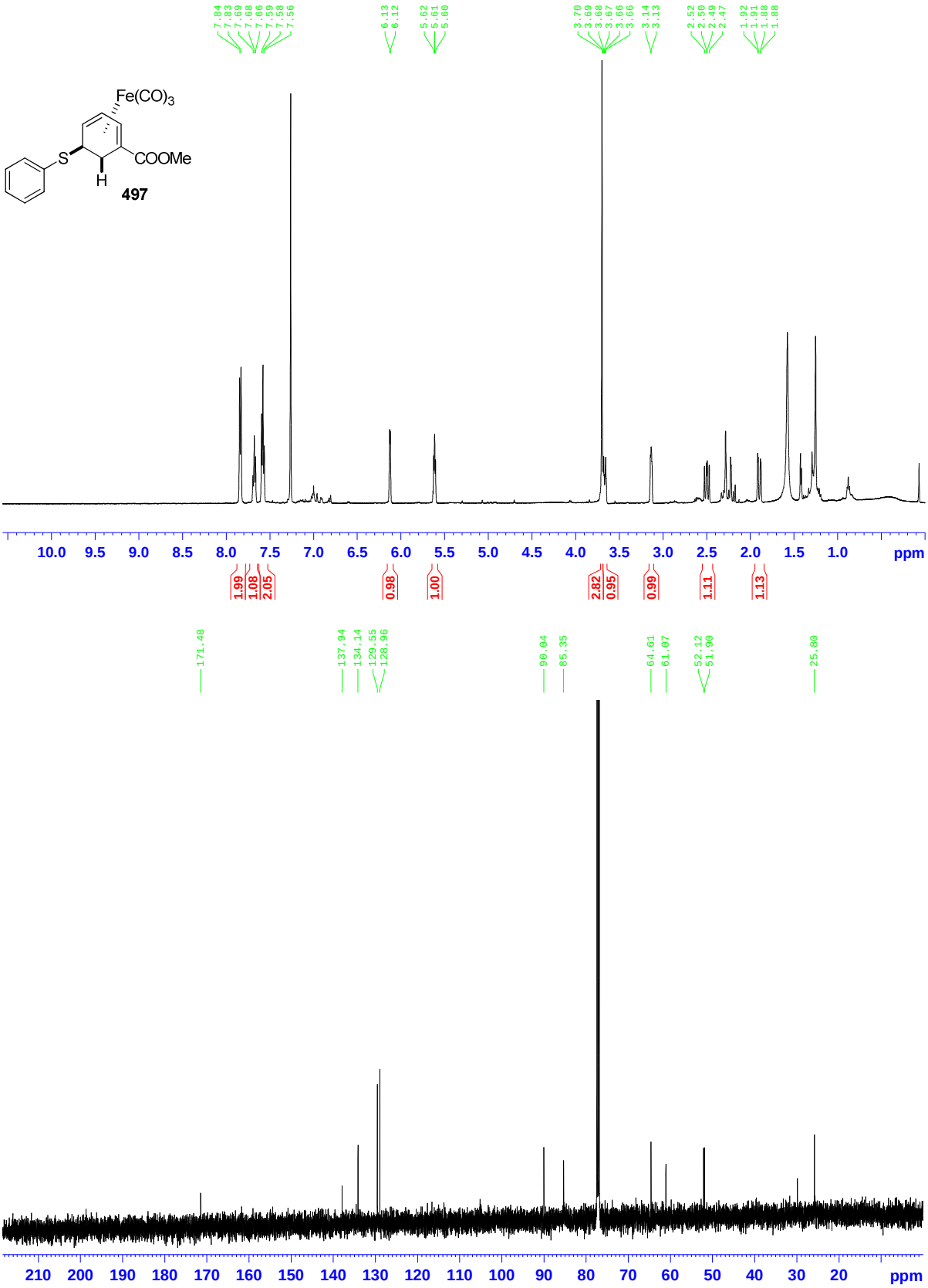
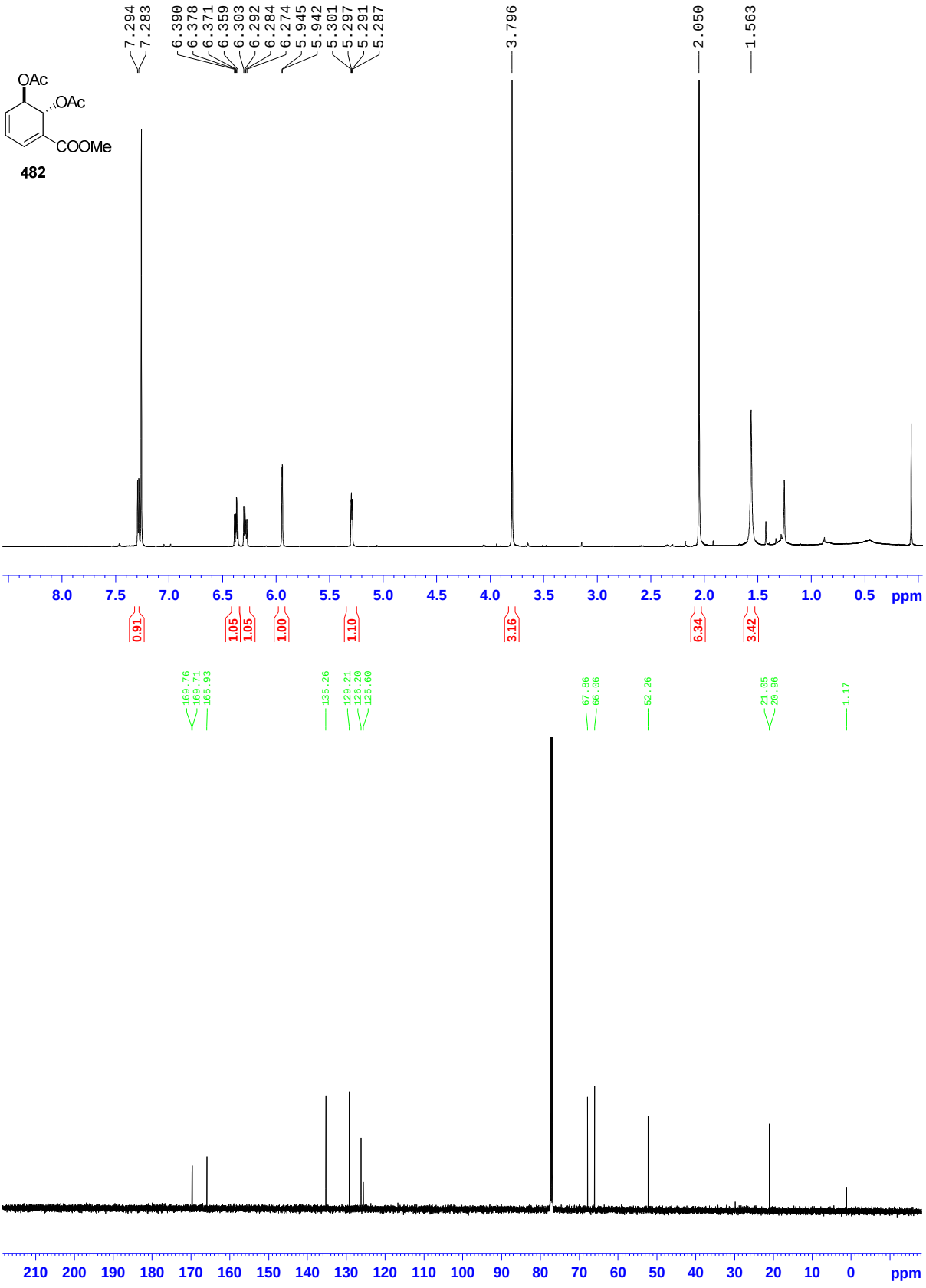
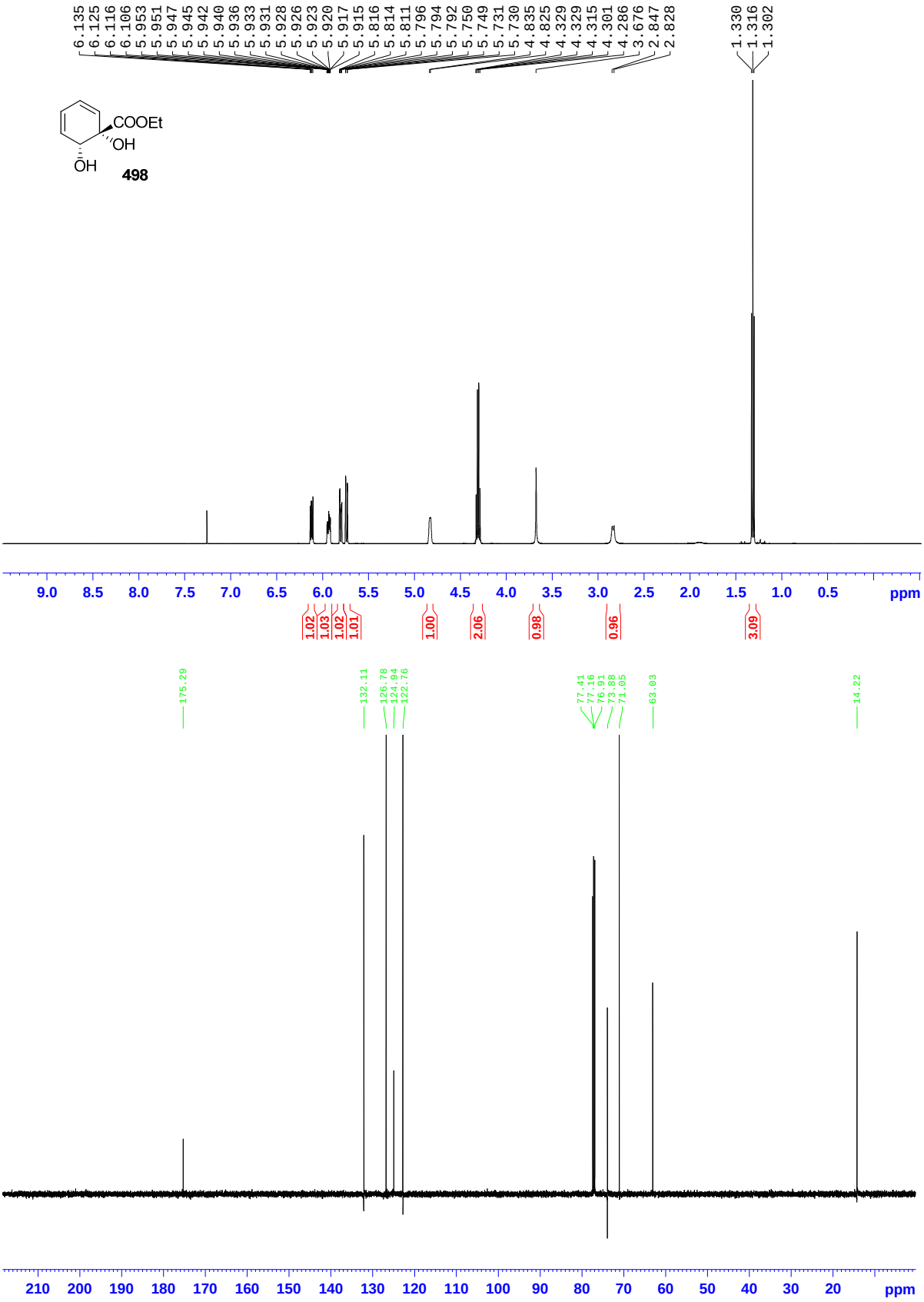
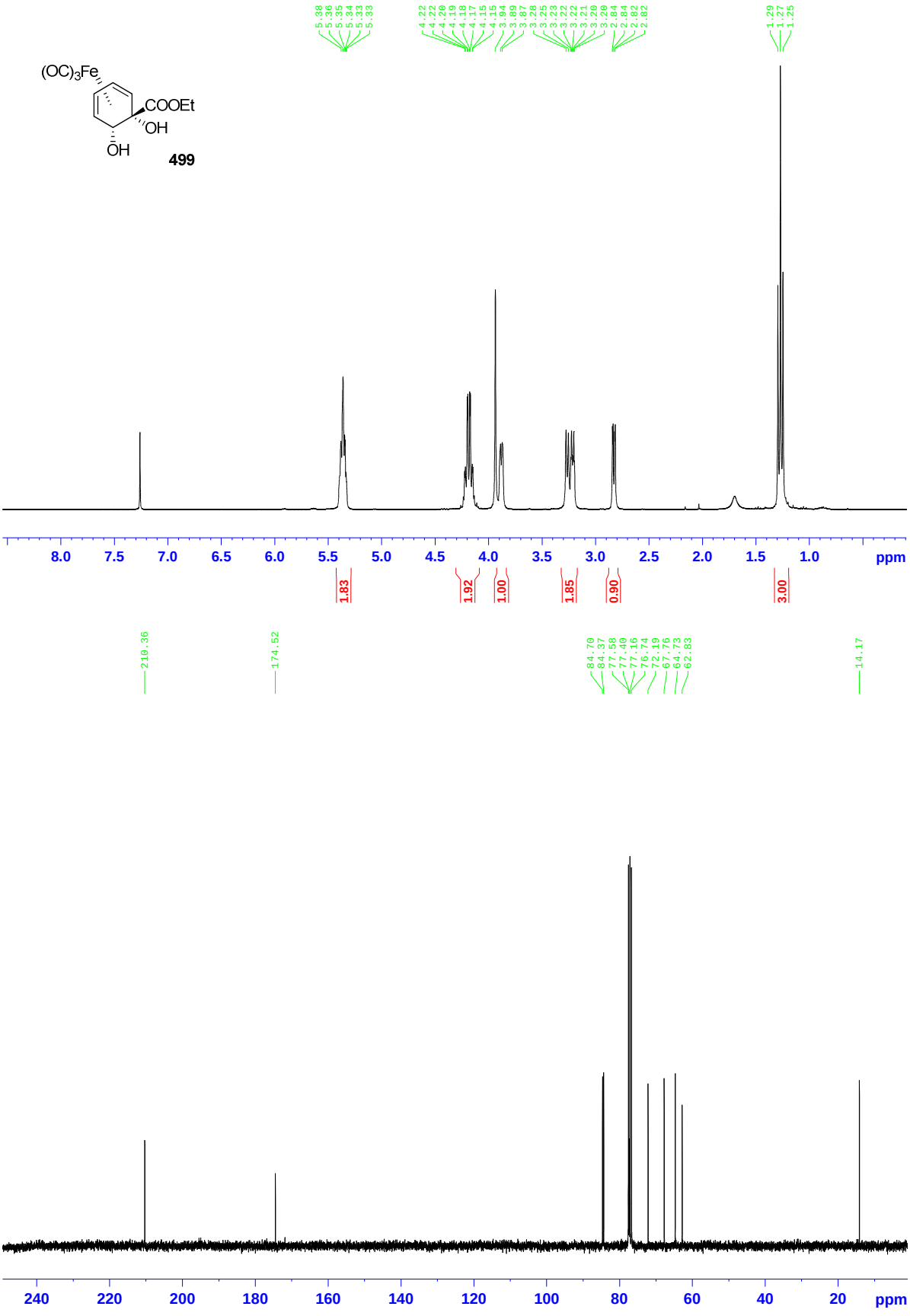
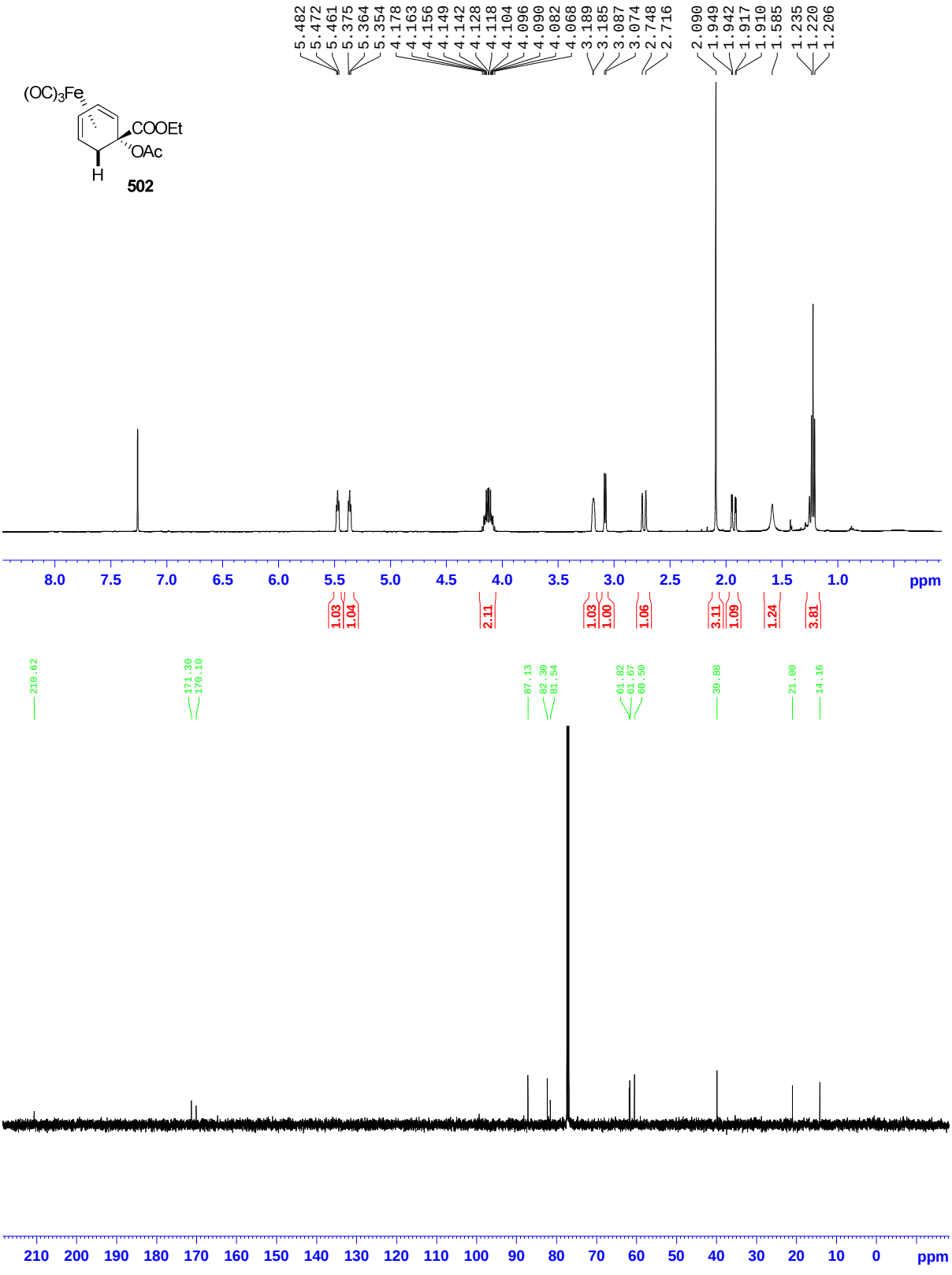
7.433
7.409
7.343
7.322
7.296
7.285
7.252
6.126
6.111
5.449
5.429
5.413
4.359
4.327
4.249
4.242
4.216
4.210
3.684
3.466
3.449
Fe(CO)3
S
COOMe
S
460
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.42
2.28
10.16
1.08
1.00
1.05
1.12
3.19
1.21
170.83
136.58
135.84
132.73
132.33
129.35
128.93
127.70
127.50
86.18
85.89
65.10
63.32
55.00
51.92
49.82
220 200 180 160 140 120 100 80 60 40 20 ppm

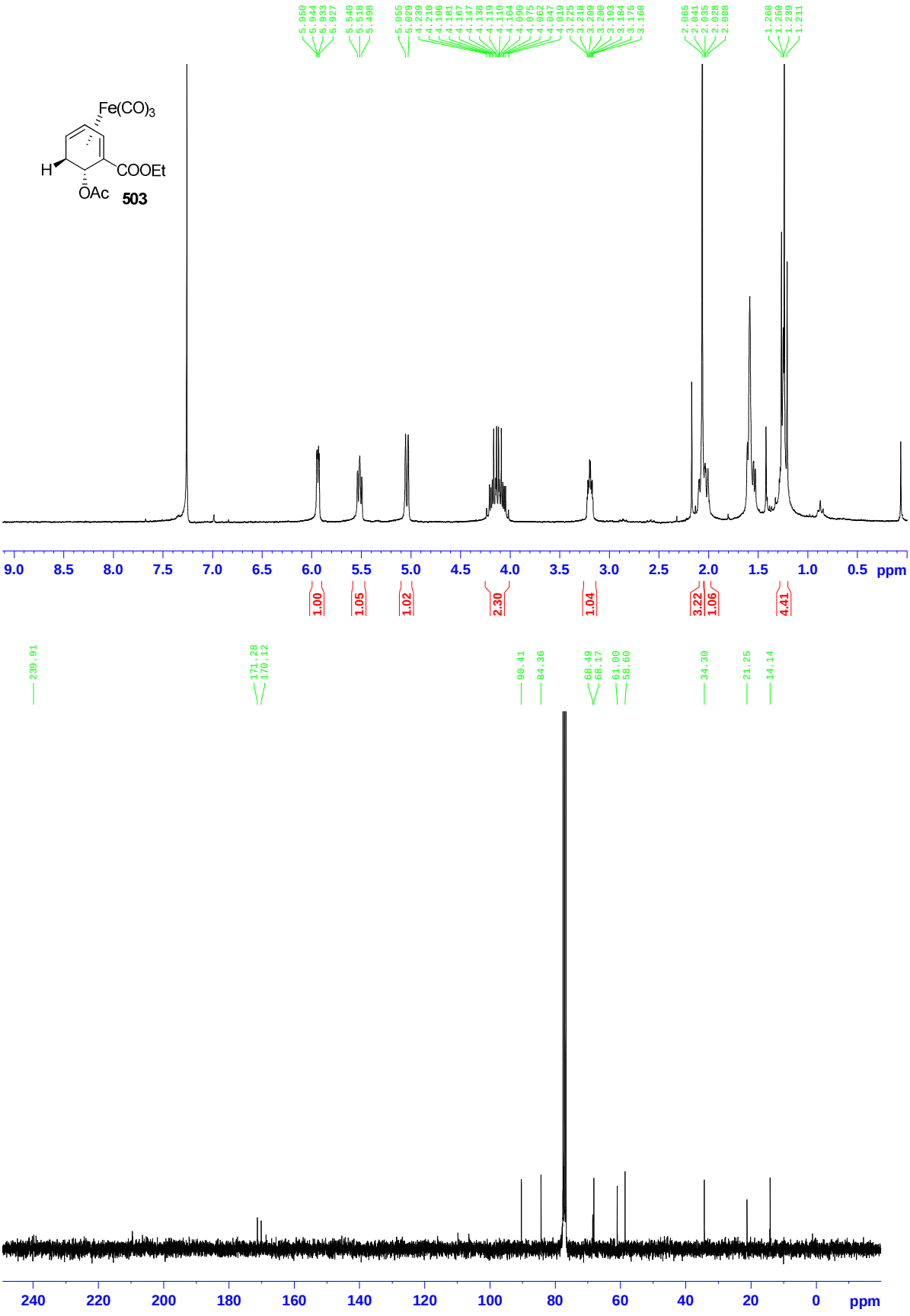

7.84
7.83
7.69
7.68
7.66
7.59
7.58
7.56
6.13
6.12
5.62
5.61
5.60
3.70
3.69
3.68
3.67
3.66
3.66
3.14
3.13
2.52
2.50
2.49
2.47
1.92
1.91
1.88
1.88
Fe(CO)3
S
COOMe
H
497
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99
1.08
2.05
0.98
1.00
2.82
0.95
0.99
1.11
1.13
171.48
137.94
134.14
129.55
128.96
90.04
85.35
64.61
61.07
52.12
51.90
25.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

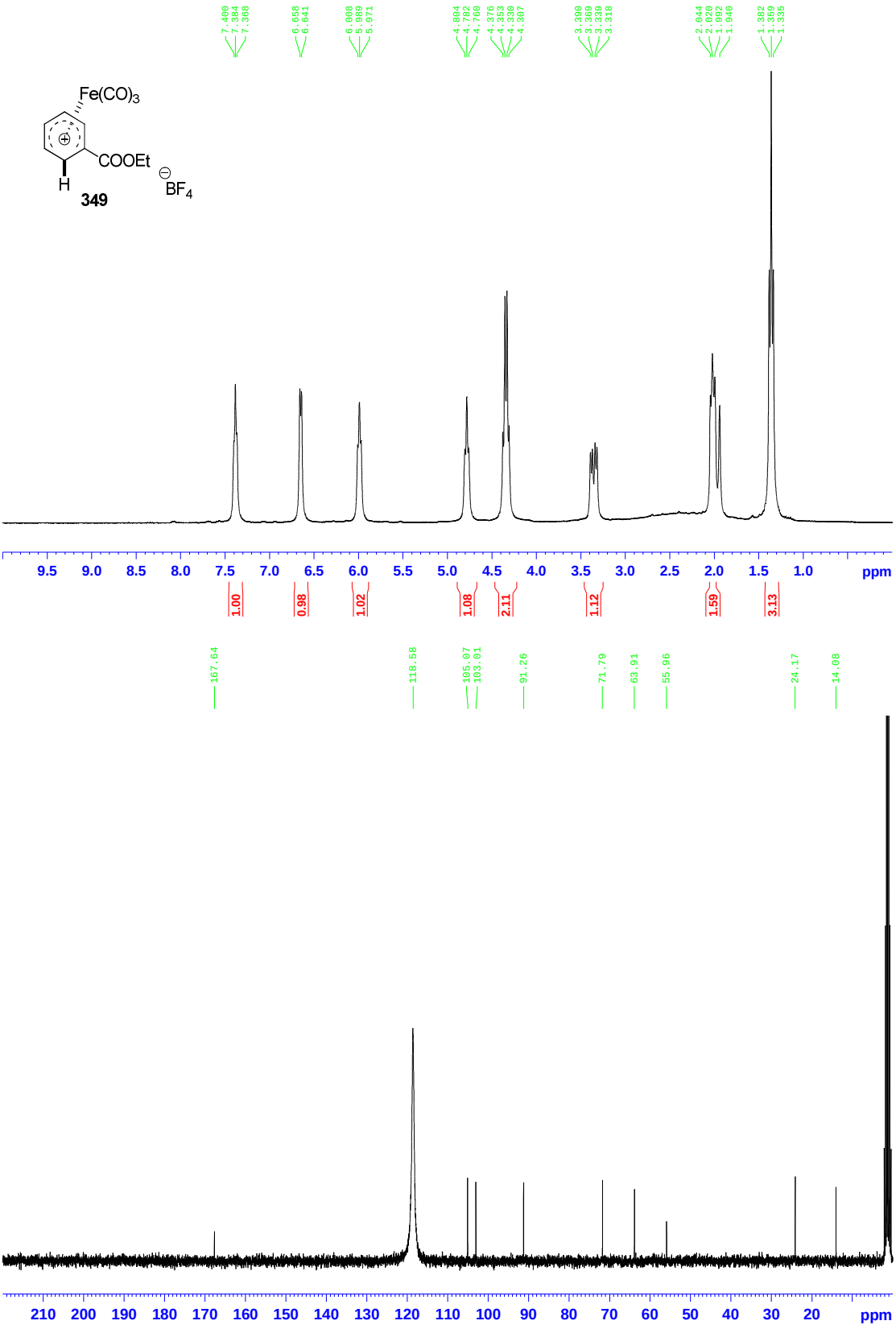

7.294
7.283
6.390
6.378
6.371
6.359
6.303
6.292
6.284
6.274
5.945
5.942
5.301
5.297
5.291
5.287
3.796
2.050
1.563
OAc
OAc
COOMe
482
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.91
1.05
1.05
1.00
1.10
3.16
6.34
3.42
169.76
169.71
165.93
135.26
129.21
126.20
125.60
67.86
66.06
52.26
21.05
20.96
1.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

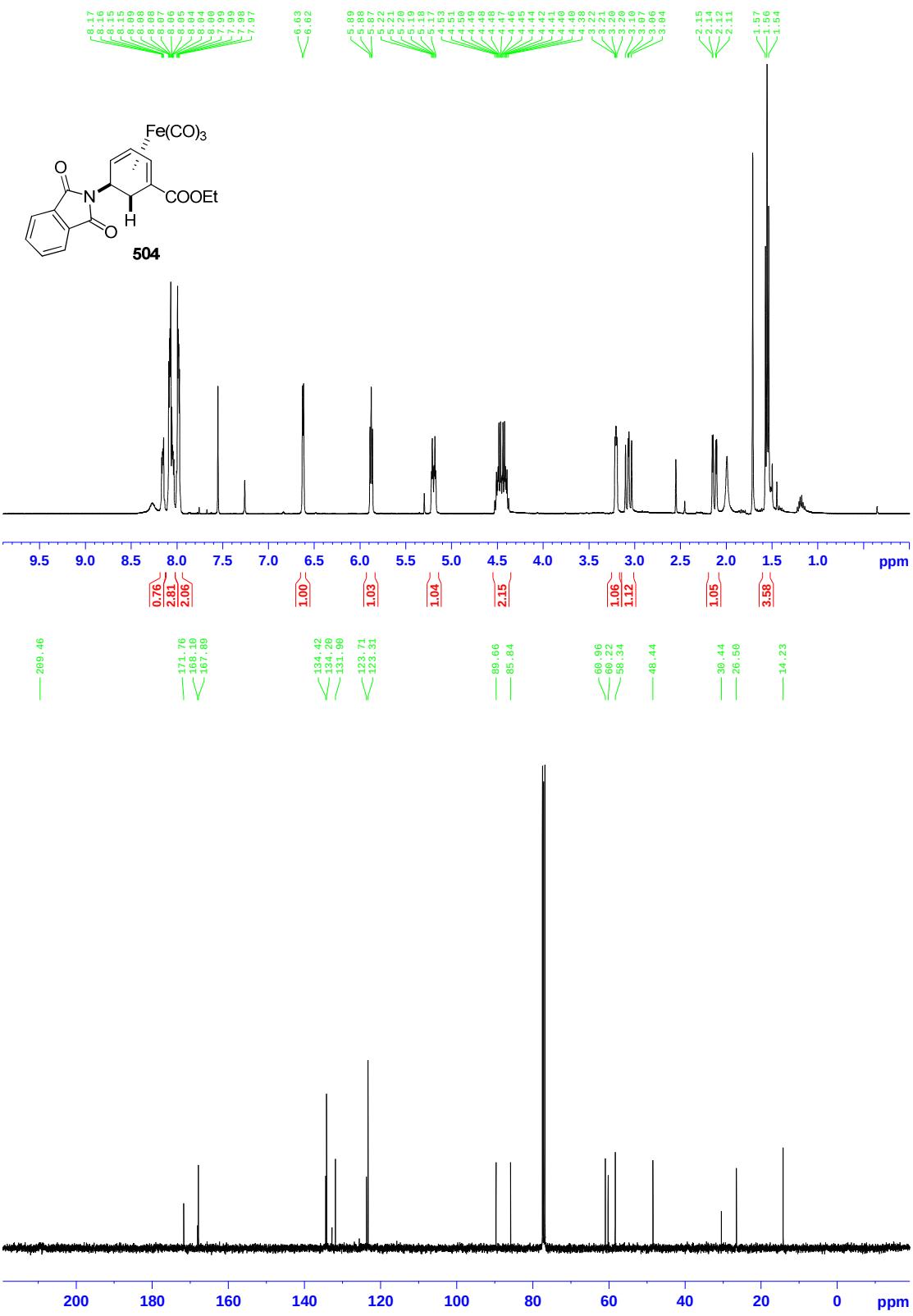

6.135
6.125
6.116
6.106
5.953
5.951
5.947
5.945
5.942
5.940
5.936
5.933
5.931
5.928
5.926
5.923
5.920
5.917
5.915
5.816
5.814
5.811
5.796
5.794
5.792
5.750
5.749
5.731
5.730
4.835
4.825
4.329
4.329
4.315
4.301
4.286
3.676
2.847
2.828
1.330
1.316
1.302
COOEt
OH
OH
498
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02 1.03 1.02 1.01 1.00 2.06 0.98 0.96 3.09
175.29
132.11
126.78
124.94
122.76
77.41
77.16
76.91
73.88
71.05
63.03
14.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

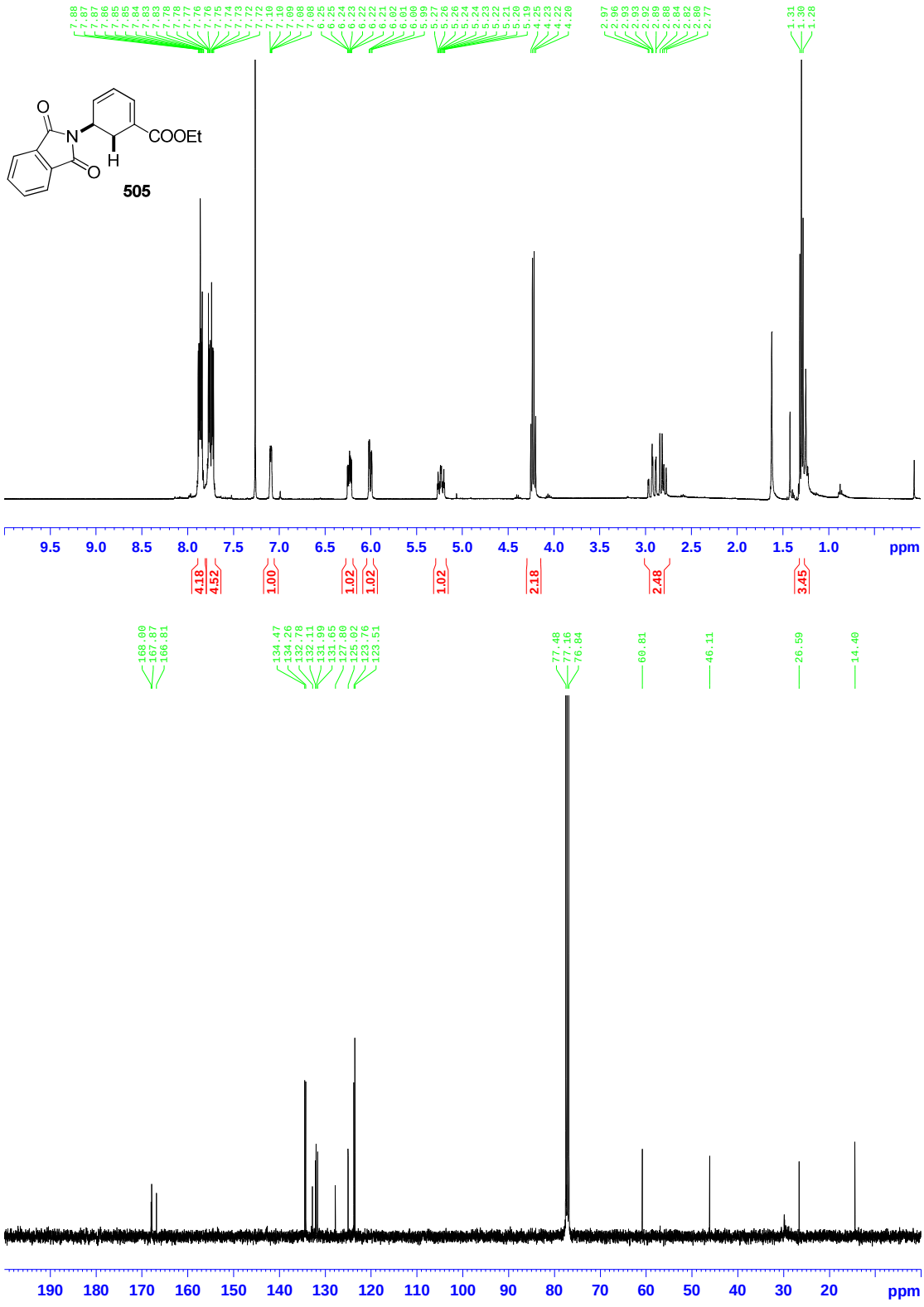

(OC)3Fe
COOEt
OH
OH
499
5.38
5.36
5.35
5.34
5.33
5.33
4.22
4.22
4.20
4.19
4.18
4.17
4.15
4.15
3.94
3.89
3.87
3.28
3.25
3.23
3.22
3.21
3.20
2.84
2.84
2.82
2.82
1.29
1.27
1.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.83
1.92
1.00
1.85
0.90
3.00
210.36
174.52
84.70
84.37
77.58
77.40
77.16
76.74
72.19
67.76
64.73
62.83
14.17
240
220
200
180
160
140
120
100
80
60
40
20
ppm

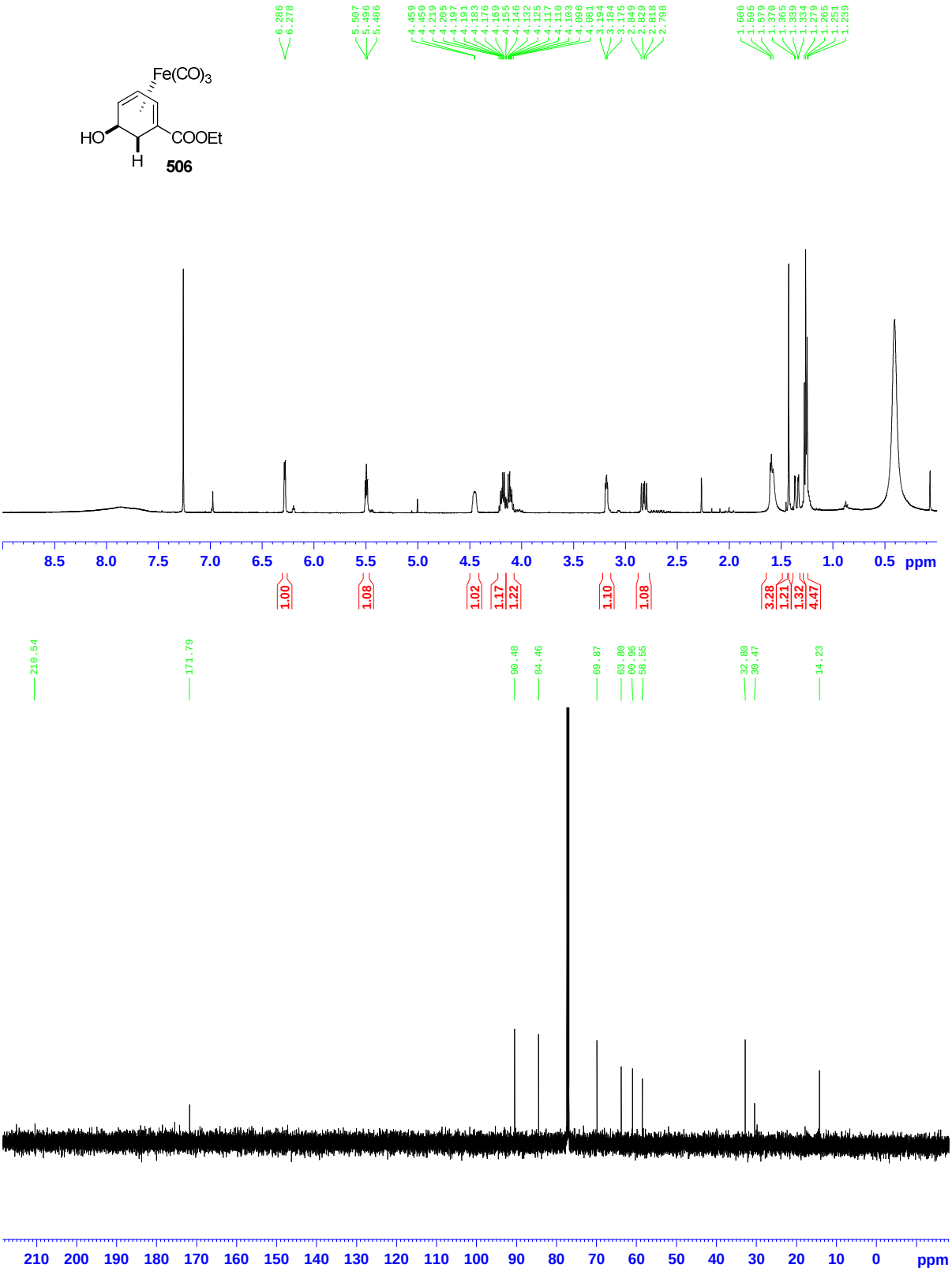

5.482
5.472
5.461
5.375
5.364
5.354
4.178
4.163
4.156
4.149
4.142
4.128
4.118
4.104
4.096
4.090
4.082
4.068
3.189
3.185
3.087
3.074
2.748
2.716
2.090
1.949
1.942
1.917
1.910
1.585
1.235
1.220
1.206
(OC)3Fe
COOEt
OAc
H
502
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.03
1.04
2.11
1.03
1.00
1.06
3.11
1.09
1.24
3.81
210.62
171.30
170.10
87.13
82.30
81.54
61.82
61.67
60.50
39.88
21.00
14.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

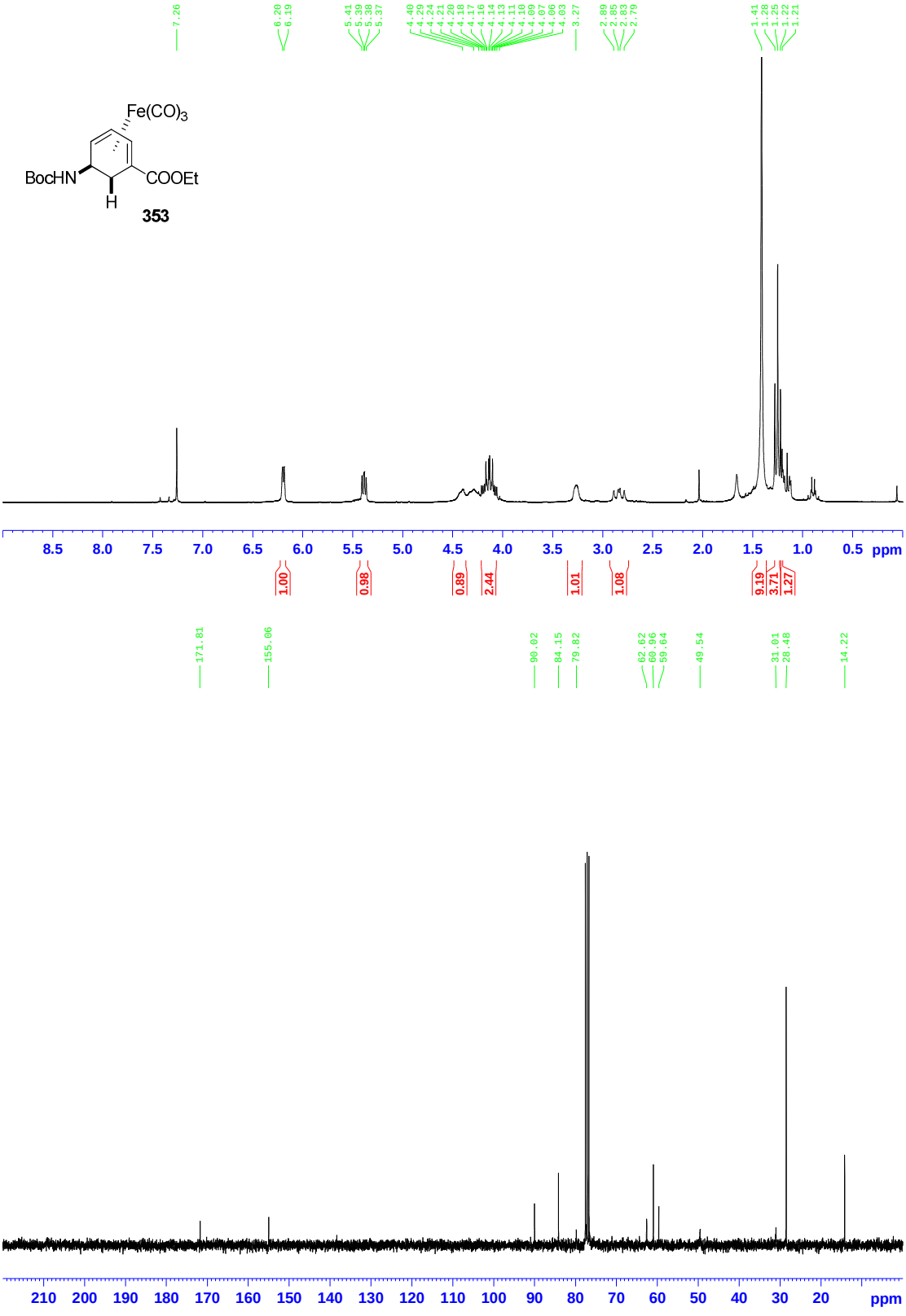

Fe(CO)3
H
COOEt
OAc
503
5.950
5.944
5.933
5.927
5.540
5.518
5.498
5.055
5.029
4.239
4.210
4.196
4.181
4.167
4.147
4.138
4.119
4.110
4.104
4.090
4.075
4.062
4.047
4.019
3.225
3.218
3.209
3.200
3.193
3.184
3.175
3.168
2.065
2.041
2.035
2.028
2.008
1.268
1.250
1.239
1.211
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.05
1.02
2.30
1.04
3.22
1.06
4.41
239.91
171.28
170.12
90.41
84.36
68.49
68.17
61.00
58.60
34.30
21.25
14.14
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

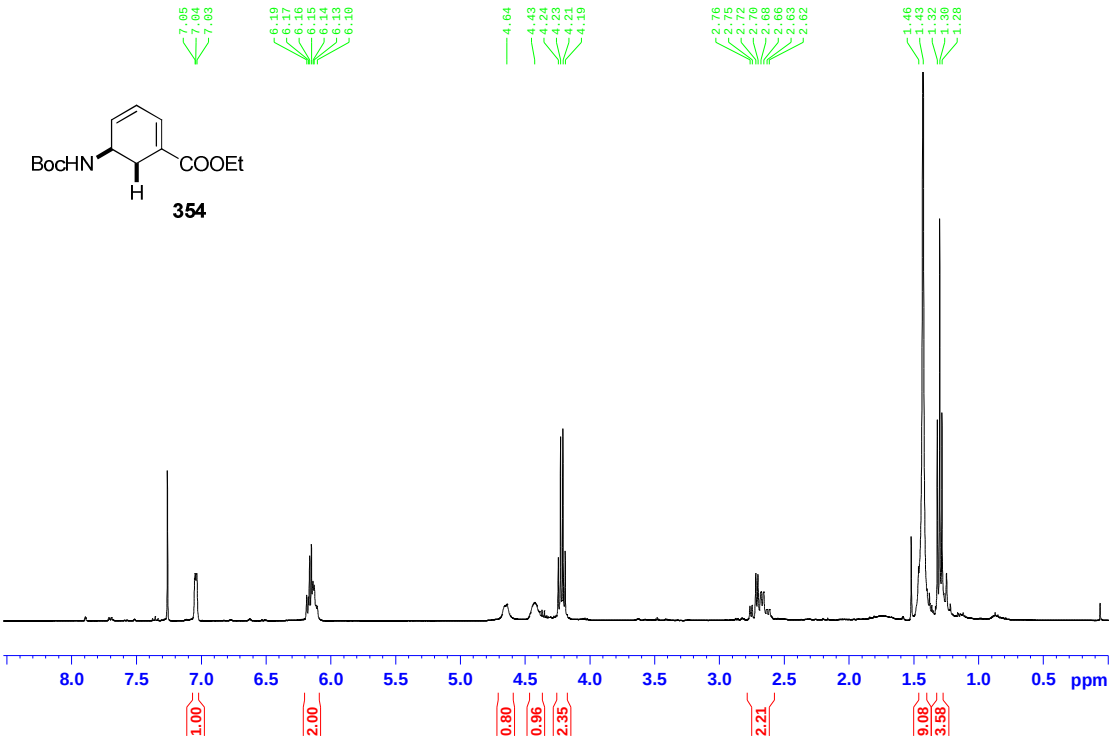

7.400
7.384
7.368
6.658
6.641
6.008
5.989
5.971
4.804
4.782
4.760
4.376
4.353
4.330
4.307
3.390
3.369
3.339
3.318
2.044
2.030
1.992
1.946
1.382
1.359
1.335
Fe(CO)3
COOEt
H
BF4
349
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
0.98
1.02
1.08
2.11
1.12
1.59
3.13
167.64
118.58
105.07
103.01
91.26
71.79
63.91
55.96
24.17
14.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

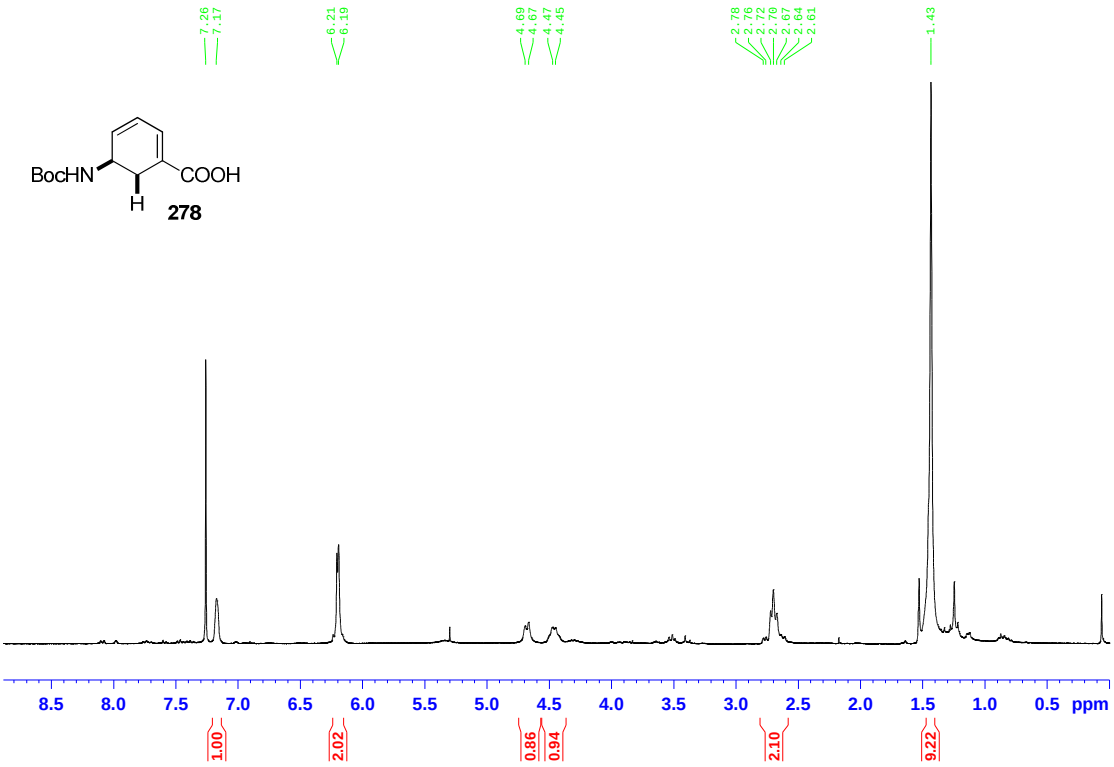

Fe(CO)3
O
N
H
O
COOEt
504
ppm
ppm

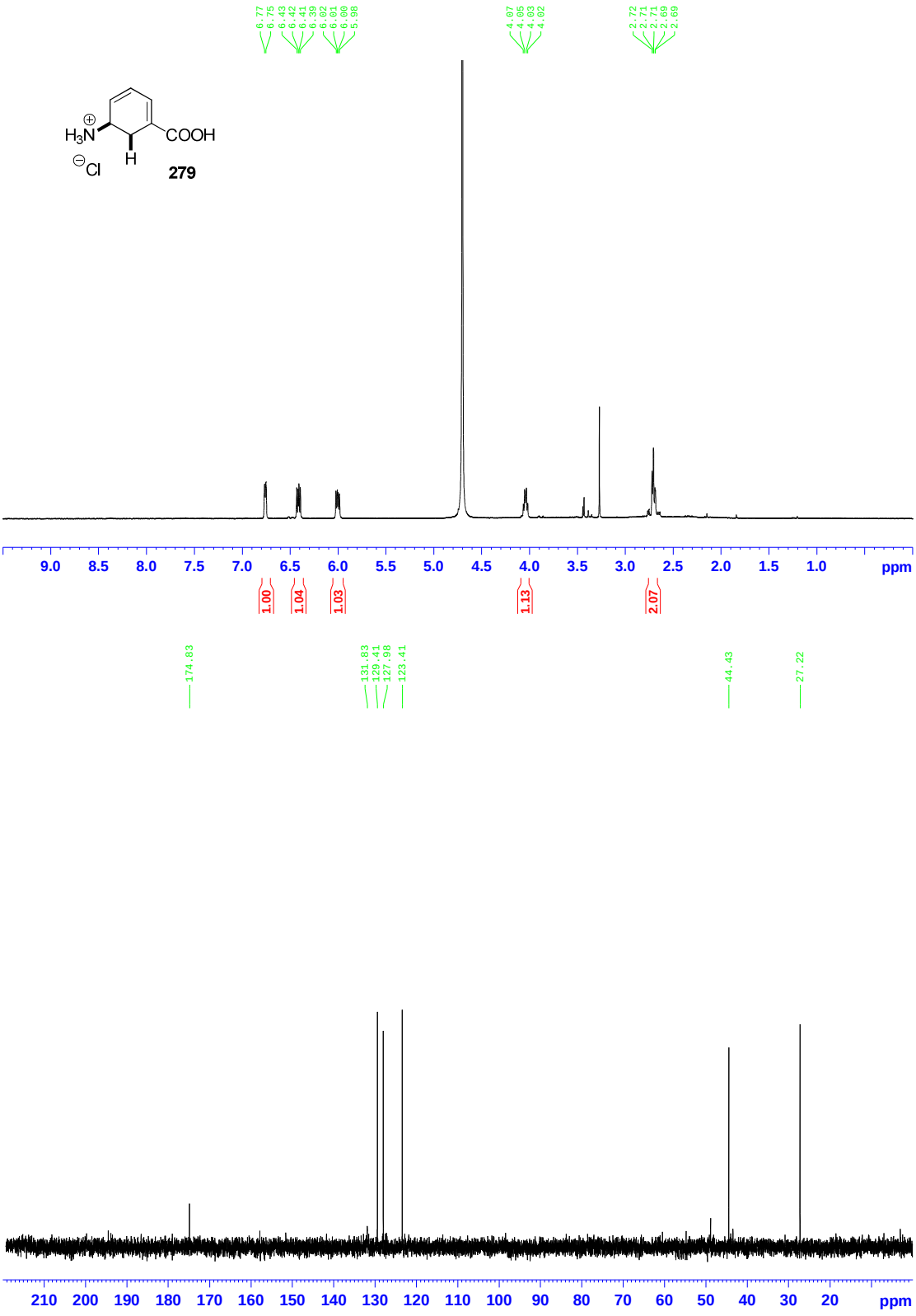

7.88 7.87 7.87 7.86 7.85 7.85 7.84 7.83 7.83 7.78 7.78 7.77 7.76 7.76 7.75 7.74 7.73 7.72 7.72 7.72 7.10 7.10 7.09 7.08 7.08 6.25 6.25 6.24 6.23 6.22 6.22 6.21 6.02 6.01 6.00 5.99 5.27 5.26 5.26 5.24 5.24 5.23 5.22 5.21 5.20 5.19 4.25 4.23 4.22 4.20 2.97 2.96 2.93 2.93 2.92 2.89 2.88 2.84 2.82 2.80 2.79 2.77 1.31 1.30 1.28
O
N
H
O
COOEt
505
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.18 4.52 1.00 1.02 1.02 1.02 2.18 2.48 3.45
168.00 167.87 166.81 134.47 134.26 132.78 132.11 131.99 131.65 127.80 125.02 123.76 123.51 77.48 77.16 76.84 60.81 46.11 26.59 14.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


6.286
6.278
5.507
5.496
5.486
4.459
4.450
4.219
4.205
4.197
4.191
4.173
4.166
4.159
4.155
4.146
4.132
4.125
4.117
4.110
4.103
4.096
4.081
3.194
3.184
3.175
2.849
2.829
2.818
2.798
1.606
1.595
1.579
1.370
1.365
1.339
1.334
1.279
1.265
1.251
1.239
Fe(CO)3
HO
COOEt
H
506
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.08
1.02
1.17
1.22
1.10
1.08
3.28
1.21
1.32
4.47
210.54
171.79
90.48
84.46
69.87
63.80
60.96
58.55
32.80
30.47
14.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Fe(CO)3
BocHN
COOEt
H
353
7.26
6.20
6.19
5.41
5.39
5.38
5.37
4.40
4.29
4.24
4.21
4.20
4.18
4.17
4.16
4.14
4.13
4.11
4.10
4.09
4.07
4.06
4.03
3.27
2.89
2.85
2.83
2.79
1.41
1.28
1.25
1.22
1.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.98
0.89
2.44
1.01
1.08
9.19
3.71
1.27
171.81
155.06
90.02
84.15
79.82
62.62
60.96
59.64
49.54
31.01
28.48
14.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.05
7.04
7.03
6.19
6.17
6.16
6.15
6.14
6.13
6.10
4.64
4.43
4.24
4.23
4.21
4.19
2.76
2.75
2.72
2.70
2.68
2.66
2.63
2.62
1.46
1.43
1.32
1.30
1.28
BocHN
COOEt
H
354
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.00
0.80
0.96
2.35
2.21
9.08
3.58


7.26
7.17
6.21
6.19
4.69
4.67
4.47
4.45
2.78
2.76
2.72
2.70
2.67
2.64
2.61
1.43
BocHN
COOH
H
278
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.02
0.86
0.94
2.10
9.22


6.77
6.75
6.43
6.42
6.41
6.39
6.02
6.01
6.00
5.98
4.07
4.05
4.03
4.02
2.72
2.71
2.71
2.69
2.69
COOH
279
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.04
1.03
1.13
2.07
174.83
131.83
129.41
127.98
123.41
44.43
27.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Appendix 3

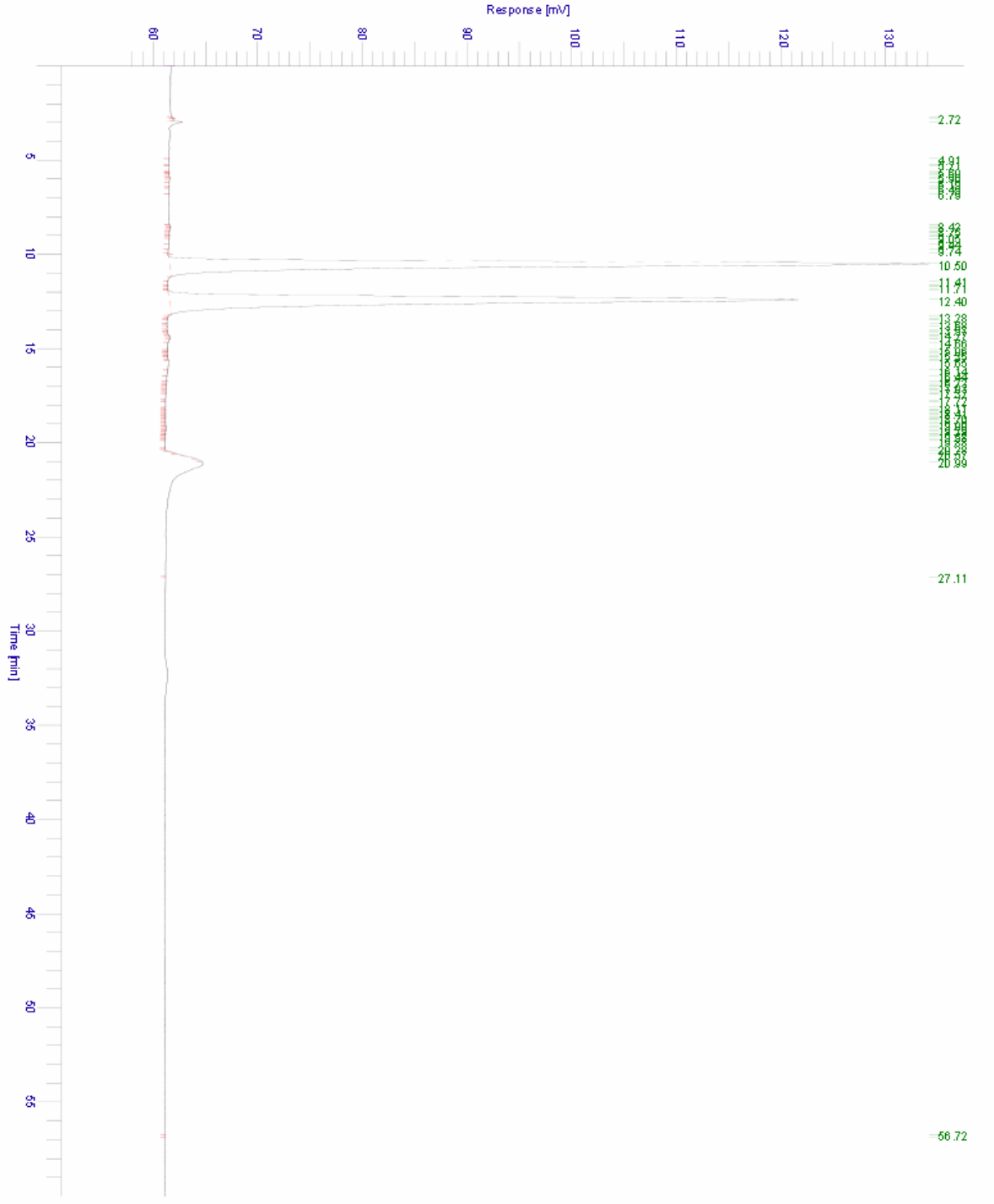
Chromatograms for 482

Chromatogram

Sample Name : Sample #: Page 1 of 1
FileName : e:\hplc\Monika280a.raw
Date : 26/01/2012 11:39:50
Method : monika280.a Time of Injection: 14/07/2011 16:30:31
Start Time : 0.00 min End Time : 60.00 min Low Point : 59.81 mAU High Point : 98.85 mAU
Scale Factor: 1.0 Plot Offset: 59.81 mAU Plot Scale: 39.0 mAU

Chromatogram

Sample Name : Sample #: Page 1 of 1
FileName : e:\hplc\Monika purge2-20110714-135046.raw
Date : 26/01/2012 11:42:46
Method : rac.monika Time of Injection: 14/07/2011 13:50:38
Start Time : 0.00 min End Time : 60.00 min Low Point : 57.43 mAU High Point : 134.17 mAU
Scale Factor: 1.0 Plot Offset: 57.43 mAU Plot Scale: 76.7 mAU



Appendix 4
Publications

1. Ali Khan, M.; Mahon, M. F.; Stewart, A. J. W.; Lewis, S. E.* **"Iron(0)tricarbonyl Complexes of Microbially-Derived Cyclohexadiene Ligands Containing Quaternary Stereocenters"** *Organometallics* **2010**, 29, 199-204. doi:10.1021/om9009069

2. Ali Khan, M.; Lowe, J. P.; Johnson, A. L.; Stewart, A. J. W.; Lewis, S. E**.*** **"Accessing the antipodal series in microbial arene oxidation: a novel diene rearrangement induced by tricarbonyliron(0) complexation"** *Chem. Commun*, **2011**, 215-217, doi:10.1039/c0cc01169j

3. Griffen, J. A.; Le Coz, A. M.; Kociok-Köhn, G.; Ali Khan, M.; Stewart, A. J. W; Lewis, S. E.* **"Expanding the chiral pool: oxidation of meta-bromobenzoic acid by *R. eutrophus* B9 allows access to new reaction manifolds**", *Org. Biomol. Chem.,* **2011**, 9, 3920–3928, doi:10.1039/c1ob05131h

4. Van der Waals, D.; Pugh, T.; Ali Khan, M.; Stewart, A.J.W.; Johnson, L.W.; Lewis, S. E.***"A Cobalt Complex of a Microbial Arene Oxidation Product",** *Chemistry Central Journal*, **2011**, Chem. Central J., **2011**, 5, 80, doi:10.1186/1752-153X-5-80

5. Ali Khan, M.; Lowe, J. P.; Johnson, A. L.; Stewart, A. J. W.; Lewis, S. E.* **"Valuable new cyclohexadiene building blocks via cationic η^5 iron carbonyl complexes derived from a microbial arene oxidation product**." *Chem. Eur. J.* **2012**, 18, 13480-13493, doi: 10.1002/chem.201202411